(η^3-allyl)Pd Complexes of Chiral N,O-Chelates: Preparation, Structures, and Prospects for Selective Allylic Functionalization

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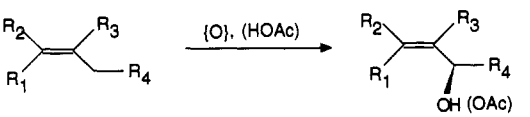
A series of (η^3-allyl)Pd derivatives of chiral N,O-bidentate ligands have been prepared and characterized to assess their potential as model intermediates for regio- and stereocontrolled catalytic allylic oxidation and substitution reactions. (*N*-(α-Methylbenzyl)salicylaldimine)-Pd(η^3-cyclohexenyl) (**5**), which exists in solution as a 1:1 Pd–allyl rotameric (*exo*/*endo*) mixture, selectively crystallizes as a single isomer. The X-ray crystal structure of this isomer of **5** (space group $P2_1$, a = 9.112(2) Å, b = 10.021(3) Å, c = 22.926(5) Å, Z = 4, R = 0.068, R_w = 0.094) shows nearly symmetrical Pd–allyl bonding parameters and the *N*-α-phenyl group *endo* to the flap of the cyclohexenyl ring. The new chiral 4-substituted salicyloxazoline ligands **3a–j** and the corresponding (salicyloxazoline)Pd(η^3-cyclohexenyl) complexes **7a–j** have been prepared in good yields by treatment of {(η^3-cyclohexenyl)PdCl}$_2$ with K[**3a–j**]. Solution NMR studies of **7a–j** indicate that the ratio of isomers is a function of the size of the α-N substituent, with single isomers being present for R = *tert*-butyl (**7d,f,h,j**). X-ray analysis of **7d** (space group $P2_12_12_1$, a = 11.074(3) Å, b = 15.596(4) Å, c = 10.195(3) Å, Z = 4, R = 0.019, R_w = 0.025) reveals that the *tert*-butyl group and the cyclohexenyl flap are in an *exo* relationship with little evidence for a differential ground-state trans influence derived from the unsymmetrical chelate. The terminal allylic proton NMR resonances of **7d,f,h,j** are separated by ca. 0.4–0.5 ppm, suggesting different electronic characters for the two allylic carbons. Reactivity studies show that the complexes **7a–j** are relatively unreactive toward HOAc, giving varying amounts of allylic acetate, and toward the nucleophiles OAc^- and $CH(CO_2CH_3)_2^-$.

Introduction

Among the methods for the synthesis of enantiomerically enriched compounds, enantioselective reactions of achiral or racemic starting materials promoted by chiral catalysts are ideal. The most successful examples of such reactions include those involving transition-metal catalysts bound to chiral chelating ligands—e.g. the Sharpless epoxidation of allylic alcohols,[1] asymmetric hydrogenation of aminocinnamic acid esters[2] and ketones,[3] and asymmetric isomerization of allylamines.[4] Because of the prior prevailing interest in catalytic reductions, much of the effort in the design and synthesis of chiral ligands has centered on chiral phosphines.[5] However, as indicated by the recent reports of asymmetric dihydroxylation[6] and epoxidation of nonfunctionalized olefins,[7] there appears to be tremendous potential for the development of asymmetric oxidation processes as well. Such catalytic reactions will require the availability of nonoxidizable (i.e. other than phosphine) ligands capable of stabilizing higher oxidation state metals.

In this connection we have been interested recently in the development of catalysts for asymmetric allylic oxidation (eq 1). Since achiral versions of these reactions are



(1)

catalyzed by Cu(I,II)[8] and Pd(II) salts,[9] we have considered the prospect of developing asymmetric variants by incorporating suitable chiral ligands on the metal. Prior limited studies of Cu-promoted stoichiometric[10] and catalytic[11] asymmetric acetoxylations reported low to moderate enantioselectivities. Mechanistically, the Pd-catalyzed allylic oxidations appear to proceed by either (η^3-allyl)Pd/acetate attack and/or by acetoxypalladation/β-Pd–H elimination pathways,[9] depending on the olefin substrate (eq 2).

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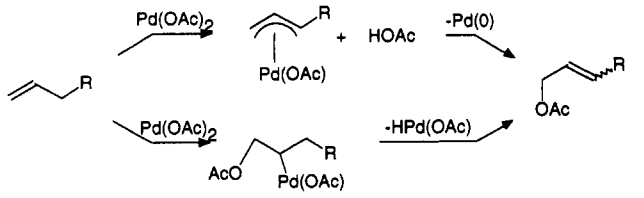
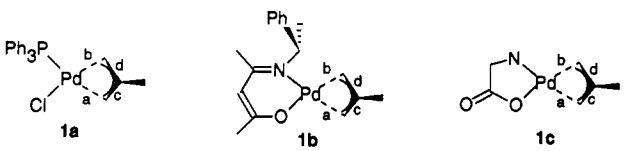


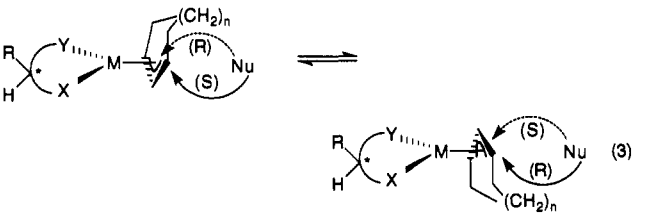
(2)

To the extent that the η^3-allyl pathway is involved in the Pd-catalyzed reactions, achieving regio- and stereocontrol in allylic oxidation may be related to the issue of selectivity in allylic *substitution* reactions. Despite considerable effort in the area[12] and some limited success,[13] an effective, general approach to regio- and stereocontrolled catalytic allylic functionalization is still lacking. Prior studies of two classes of complexes, however, provide a basis for addressing simultaneously the general regioselectivity problem and for designing enantioselective allylic functionalization catalysts. Faller and co-workers elegantly demonstrated the feasibility of chemically differentiating the ends of a symmetrical η^3-allyl ligand through electronic asymmetry at a metal center using chiral CpMo(NO)CO(η^3-allyl) complexes.[14] These compounds exist as equilibrating *endo* and *exo* isomers, both of which undergo regiospecific attack by nucleophiles (at markedly different rates) on the allylic carbon *cis* to the more strongly π-accepting NO ligand and stereospecifically *anti* to the Mo. The electronic origin of this ligand-induced electronic asymmetry effect has been analyzed theoretically by Hoffmann and Faller[15] and later by Curtis and Eisenstein[16] for related (diphos)Cl(CO)$_2$Mo(allyl) complexes.

More relevant to potential systems for catalytic allylic oxidation are (η^3-allyl)PdLL′ (L = L′) complexes which feature inequivalent terminal allyl carbons by virtue of electronically different ligand donor atoms. X-ray diffraction studies of such complexes, e.g. **1a–c**,[17–19] have

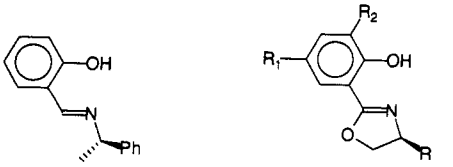


revealed a variable degree of unsymmetrical coordination to the allyl fragment, as reflected by comparison of the M–C$_{terminal}$ and, sometimes, the C–C$_{allyl}$ bond lengths. In structures **1a,b** the longer Pd–C distance is *trans* to the donor atom of greater *trans* influence, i.e. P > Cl$^-$ and N > O$^-$,[20] whereas in **1c** the allyl unit is nearly symmetrically bonded to Pd. Electronic asymmetry within the allyl ligand of the amino ketonate derivatives **1b** is also suggested by their ^{1}H NMR spectra,[18] in which the pairs of terminal allylic proton resonances are widely separated ($\Delta\delta$ ca. 0.5–0.9 ppm), but this effect may in part reflect anisotropic shielding by the *N*-benzyl group. If this apparent unsymmetrical electronic character were reflected in reactions of these complexes, it could offer a general strategy for achieving regio- and stereocontrol in allylic substitution and oxidation reactions. Unfortunately, reactivity studies of such unsymmetrical allyl derivatives have been very limited and, despite some rather high regioselectivities observed in malonate additions to certain LL′Pd(η^3-allyl) complexes,[21] the results have not been exploited synthetically. The LL′Pd(η^3-allyl) complexes, like the above Mo counterparts, also can exist as "*exo*" and "*endo*" M–allyl rotational isomers whose rate of interconversion is slow on the NMR times scale.[18,22] As noted earlier, this phenomenon may have a critical impact on the net *stereoselectivity* of nucleophilic attack, since even if attack at a particular allylic carbon is directed stereospecifically by the differential trans effect of X vs Y (eq 3), the presence of both isomers could still result in cancellation of stereoselectivity, i.e. racemic product.



(3)

In the design of potential catalysts for asymmetric allylic oxidation a number of general requirements should be met: (1) the chiral catalyst should retain the redox and electronic properties of the known achiral catalysts, (2) the ligand should be inert to oxidation, (3) the chiral ligand should be coordinated during the stereoinducing step, and (4) the ligand should induce significant and controllable asymmetry at the metal–substrate unit. On the basis of these considerations we have prepared and characterized a series of *chiral, unsymmetrical* bidentate N,O-ligands (L*), derived from salicylaldehyde, aldimine derivative **2**, and oxazoline derivatives **3**, and the corresponding (η^3-allyl)PdL* complexes in order to assess their potential for directing regio- and stereocontrolled reactions at the allyl unit.



2 **3**

We note that substituted 2-oxazolines have been utilized as effective chiral auxiliaries in organic synthesis for some

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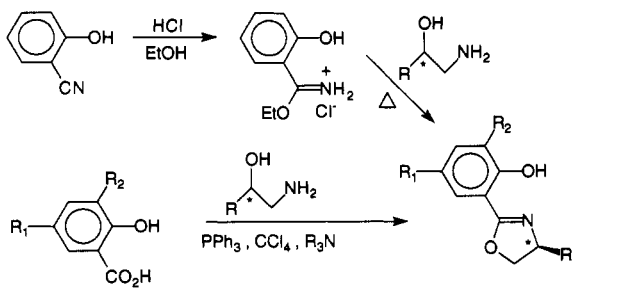
time.[23] However, metal derivatives based on chelating oxazolines have only very recently received attention[24] as chiral catalysts. A few metal chelates of *achiral* 2-(2′-hydroxyphenyl)-2-oxazolines have been prepared,[25] but neither their chemistry nor their catalytic activity have been examined. We report herein the first chiral members of this ligand class and several Pd(η^3-allyl) derivatives, including their structural characterization and initial reactivity studies.

Results and Discussion

Preparation of Ligands. (*R*)-*N*-(α-Methylbenzyl)-salicylaldimine (**2**) was readily prepared by the condensation of salicylaldehyde with (*R*)-α-methylbenzylamine.[26] To provide a more rigid and well-defined stereochemistry in the Pd coordination environment, we also prepared a number of salicyl-2-oxazoline derivatives **3** derived from readily available chiral α-amino alcohols. The most often used synthetic route to 5-substituted 2-oxazolines is the cyclization of *N*-acyl α-amino alcohols using thionyl chloride.[27] However, 5-phenyl-2-(2′-hydroxyphenyl)oxazoline (**3a**) was obtained in low yield by treatment of *N*-salicyl-(*R*)-2-phenylglycinol, made from salicyl chloride and (*R*)-2-phenylglycinol, with thionyl chloride. An alternative approach, involving direct condensation of salicylic acid with (*R*)-2-phenylglycinol under basic conditions,[28] produced **3a** again in modest yield (20%), the majority of the starting materials remaining unreacted; longer reaction times did not increase the yield. This direct method is suitable, however, for the preparation of derivatives possessing electron-withdrawing substituents on the aromatic ring (*vide infra*). High yields of **3a** were eventually achieved using a modification of the method of Black[25] via condensation of ethyl 2-hydroxybenzimidate hydrochloride with (*R*)-2-phenylglycinol (eq 4). The other



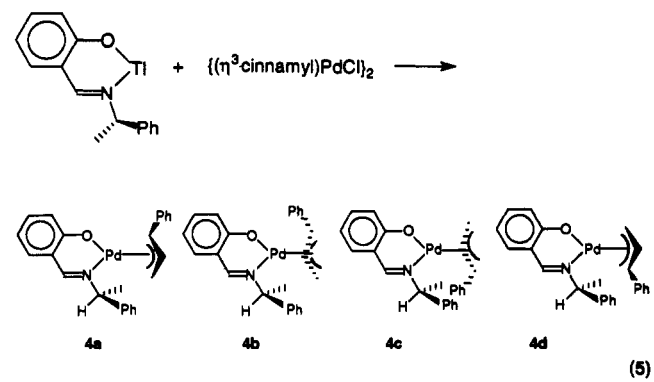
3a R_1=R_2=H, R=Ph
3b R_1=R_2=H, R=$CO_2CH(CH_3)_2$
3c R_1=R_2=H, R=$CH(CH_3)CH_2CH_3$
3d R_1=R_2=H, R=$C(CH_3)_3$
3e R_1=NO_2, R_2=H, R=Ph
3f R_1=NO_2, R_2=H, R=$C(CH_3)_3$
3g R_1=R_2=NO_2, R=Ph
3h R_1=R_2=NO_2, R=$C(CH_3)_3$
3i R_1=OCH_3, R_2=H, R=Ph
3j R_1=OCH_3, R_2=H, R=$C(CH_3)_3$

(4)

5-substituted (2′-hydroxyphenyl)-2-oxazolines (**3a–d**) were made similarly (60–80% yield) by reaction of 2-hydroxybenzimidate (or its hydrochloride) with the appropriate amino alcohol hydrochlorides (or the free amines). All of these new compounds were obtained in analytically pure form as low-melting, moisture-sensitive white solids and have been fully characterized spectroscopically.

In order to provide a set of chiral, bidentate ligands with variable electronic characteristics, we also prepared a number of 5′- and 3′,5′-aromatic substituted oxazolines (**3e–h**) by the CCl_4/PPh_3-promoted[29] direct reaction of the appropriate salicylic acid with amino alcohols according to eq 4. Moderate yields (20–70%) of these white or pale yellow crystalline solids were thus obtained and characterized spectroscopically.

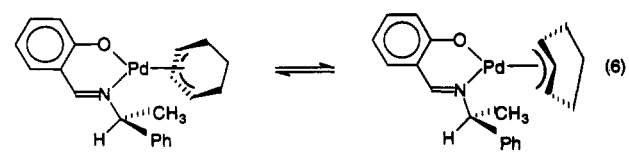
Preparation and Properties of (η^3-allyl)PdL$^+$ Complexes. Our initial efforts centered on the study of unsymmetrical cinnamyl derivative **4** in order to potentially probe regio- and stereocontrol simultaneously. Complex **4** was obtained as yellow microcrystals from the reaction of the dimeric cinnamyl complex [(η^3-PhCHCHCH$_2$)$PdCl_2]_2$[30] and the thallium salt of (α-methylbenzyl)salicylaldimine (eq 5). As synthesized, **4** was found to



(5)

be a mixture of four isomers (**4a–d**, one major pair and one minor pair), as indicated by ^{1}H NMR spectroscopy. The complexity of the spectra prevented unambiguous assignment of the resonances to the individual isomers; attempted separation by HPLC on silica was unsuccessful. We suspect that the major isomers **4a,b** (rotamers) have the allyl CH–Ph and chelate NR groups in the less hindered *trans* relationship and differ according to which face of the prochiral cinnamyl unit is coordinated. Real-time monitoring by variable-temperature NMR between −85 and +50 °C revealed no change in the isomer ratio, indicating very slow (if any) interconversion.

To simplify matters, we turned our attention to synthesizing a (**2**)Pd^{II} derivative of a representative *symmetrical* allyl unit, i.e. η^3-cyclohexenyl complex **5** (eq 6).



5a (*exo*) **5b** (*endo*) (6)

In this case we found it advantageous to use yellow, soluble [(η^3-cyclohexenyl)$PdCl_2]_2$ (**6**), produced from 3-cyclohex-

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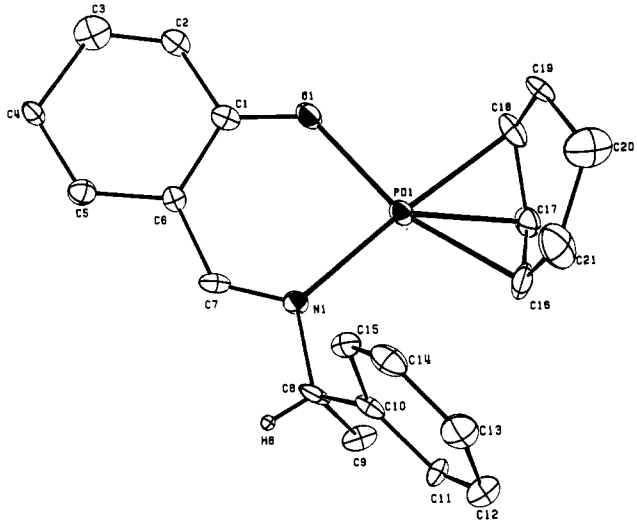

Figure 1. ORTEP structure of **5a** (only one of two independent molecules shown).

Table I. Selected Bond Lengths (Å) and Angles (deg) for 5a

Pd–O1	2.068(9)	O1–C1	1.317(17)
Pd–N1	2.093(9)	N1–C8	1.536(15)
Pd–C16	2.172(15)	C1–C6	1.377(18)
Pd–C17	2.102(13)	C6–C5	1.440(18)
Pd–C18	2.148(12)	C6–C7	1.435(24)
C16–C17	1.417(18)	C7–N1	1.323(24)
C17–C18	1.370(18)		
C18–Pd–O1	96.1(4)	O1–C1–C6	124.2(13)
C16–Pd–N1	106.8(4)	C1–C6–C7	126.9(13)
O1–Pd–N1	90.1(4)	C6–C7–N1	127.4(13)
C16–Pd–C18	66.8(5)		

enyl chloride,[30] as the starting material since an alternative procedure using cyclohexene in acetic acid[31] largely afforded a red, sparingly soluble, less reactive (presumably isomeric) form of **6**. The desired η^3-cyclohexenyl complex **5** was obtained as a yellow solid in high yield by treating a mixture of (α-methylbenzyl)salicylaldimine and the yellow form of **6** with potassium *tert*-butoxide in toluene. The ^{1}H NMR spectrum of **5** at room temperature exhibited pairs of resonances for a number of the protons, suggesting the presence of two isomers (ca. 1:1, **5a,b**). Slow crystallization of **5a,b** from toluene–hexane solution (–20 °C, 3–5 days), however, afforded a high recovery (80%) of large greenish yellow single crystals of **5a**, one of which was used for X-ray structure determination (Figure 1, Table I). Two nearly identical independent molecules are found in the asymmetric unit (only one shown) of **5a**. Each molecule exhibits a distorted-square-planar environment about the Pd atom defined by the N,O atoms of the chelating ligand and the terminal carbons (C7,17) of the allyl fragment. In contrast to the structure of salicylaldimine derivative **1b**, in which a substantially longer Pd–C bond is found trans to N vs trans to O,[18] little indication of a differential ground-state trans influence of the unsymmetrical chelate on the allyl fragment of **5** is seen; i.e., Pd–C18 (trans to N, 2.18 Å) = Pd-C16 (trans to O, 2.17 Å). However, a similar substantial angular distortion of the Pd–chelate relative to the Pd–allyl unit is present in both structures; e.g. C16–Pd–N1 = 107° vs C18–Pd–O1 = 96° for **5** vs corresponding angles of 106.6 and 94.6° in **1b**. This distortion may reflect a steric repulsion between the η^3-cyclohexenyl and α-phenyl groups of the latter.[18] Also interesting is the contrast in the structure of the Pd–chelate ring: in **1b** alternating bond lengths within the chelate indicate localized bonding, whereas bond alternation in the chelate ring of **5a** is much less pronounced, consistent with a more delocalized structure. This effect could mediate the difference in *trans* influence of the N- and O-donor atoms in complex **5a**. Two features of the structure of the latter also are seemingly contrasteric, namely the *endo* relationship of the flap of the cyclohexenyl ring and the α-phenyl group and the conformation of the *N*-α-methylbenzyl group, which directs the Me and Ph groups toward the Pd–cyclohexenyl unit.

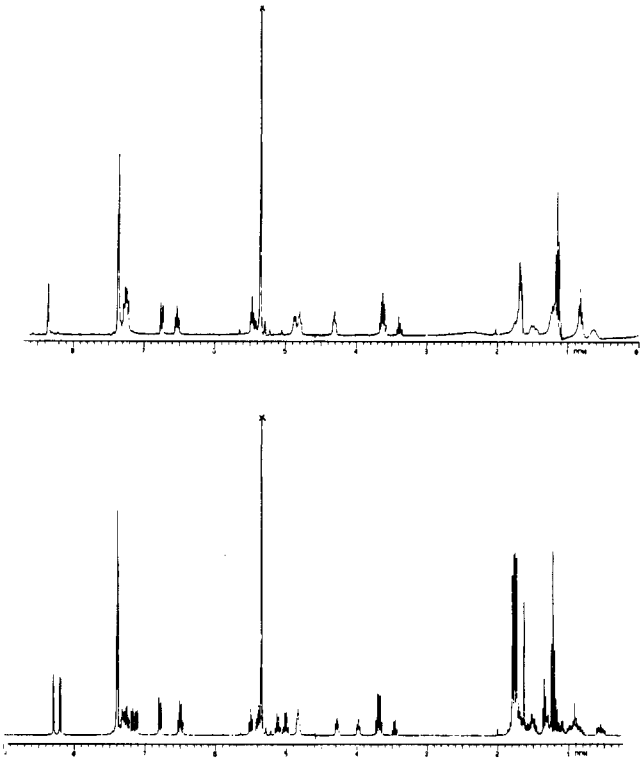

Figure 2. ^{1}H NMR spectra of **5a** in CD_2Cl_2: (a, top) spectrum obtained by dissolution and recording at –78 °C; (b, bottom) after warming to 20 °C. × denotes CH_2Cl_2 impurity.

To address this issue and the interesting observation that most (ca. 80%) of the original 1:1 solution isomer mixture crystallizes as a single isomer, crystals of **5a** grown at low temperature (as for the X-ray determination) were redissolved at –78 °C and the ^{1}H NMR spectrum recorded at this temperature (Figure 2a). Indeed, the resulting spectrum (Figure 2a) clearly showed only a single isomer to be present, presumably the same as in the crystalline state. When the solution was warmed to ca. –20 °C, the resonances of another isomer, **5b**, generally appearing at higher field than those of the initial one, began to emerge, reaching a 1:1 ratio at room temperature (Figure 2b). This ratio remained unchanged (during NMR monitoring) upon further warming to 50 °C or after recooling to –85 °C. The crystallization and NMR behavior indicates that the interconversion of **5a** and **5b** is slow on the NMR time scale. This conclusion was supported by magnetization transfer experiments: e.g., saturation of the azomethine

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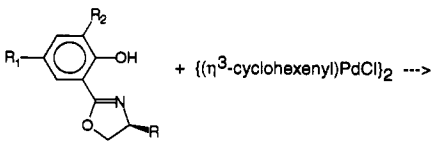
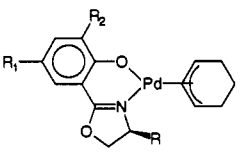
singlet of one isomer produced no transfer of magnetization to the corresponding resonance of the other isomer. The selective crystallization of *endo*-**5a** would thus appear to reflect its lower solubility (and greater crystal packing forces) rather than a greater thermodynamic stability relative to the *exo* isomer **5b**.

The C–N rotational flexibility present in **5** was presumed to be responsible for the energetic accessibility of the two Pd–allyl rotamers **5a,b** (no mechanism of interconversion implied). Accordingly, we sought to prepare a series of related bicyclic chelate complexes in which a more rigid structure would be enforced, hopefully favoring a single isomer. Toward this objective, reaction of the potassium salt of salicyloxazolines **3a–j** with cyclohexenyl–Pd dimer **6** in toluene at room temperature produced the corresponding η^3-cyclohexenyl complexes **7a–j** in good to excellent yield (60–90%, eq 7). Complexes **7a–c** were

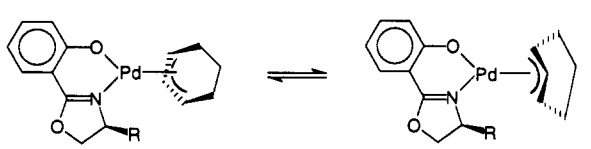




(7)

7a R_1=R_2=H, R=Ph
7b R_1=R_2=H, R=$CO_2CH(CH_3)_2$
7c R_1=R_2=H, R=$CH(CH_3)CH_2CH_3$
7d R_1=R_2=H, R=$C(CH_3)_3$
7e R_1=NO_2, R_2=H, R=Ph
7f R_1=NO_2, R_2=H, R=$C(CH_3)_3$
7g R_1=R_2=NO_2, R=Ph
7h R_1=R_2=NO_2, R=$C(CH_3)_3$
7i R_1=OCH_3, R_2=H, R=Ph
7j R_1=OCH_3, R_2=H, R=$C(CH_3)_3$

obtained as pale yellow powders upon attempted crystallization, but **7d** formed regularly shaped crystals, suggesting the presence of a single isomer in this case. This was confirmed by the proton NMR spectra of **7a,b**, which revealed the presence of a 1:1 mixture of two isomers, while *sec*-butyl derivative **7c** was a 3:2 isomeric mixture (eq 8). Generally, the resonances of the minor isomer (if



7 (*endo*) 7 (*exo*)

present) appear at higher field than the those of the major. The NMR spectra were unchanged during variable-temperature NMR experiments, indicating that isomer interconversion is slow. On the other hand, NMR spectra of the *tert*-butyl derivatives **7d,f,h,j** showed essentially a single isomer (>95%) to be present in solution.

In order to probe in detail the molecular structure of these new salicyloxazoline–M(allyl) derivatives, the molecular structure of **7d** was determined with very high precision by X-ray diffraction (Figure 3, Table II). The

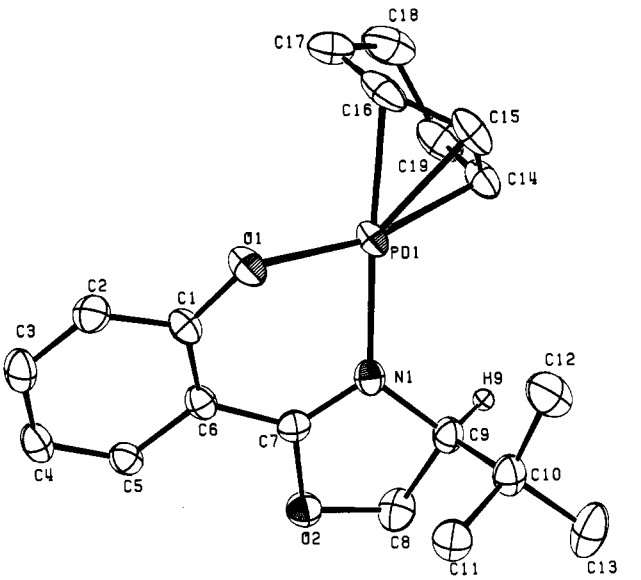


Figure 3. ORTEP structure of **7d**.

Table II. Selected Bond Lengths (Å) and Angles (deg) for 7d

Pd–O1	2.084(2)	C15–C16	1.407(6)
Pd–N1	2.078(2)	C1–O1	1.306(3)
Pd–C14	2.116(3)	C1–C6	1.413(4)
Pd–C15	2.091(3)	C6–C7	1.449(4)
Pd–C16	2.133(3)	C7–N1	1.295(3)
C14–C15	1.404(5)	C7–O2	1.353(3)
C16–Pd–O1	100.4(1)	O1–C1–C6	126.0(3)
C14–Pd–N1	103.1(1)	C1–C6–C7	121.6(2)
O1–Pd–N1	87.4(1)	C6–C7–N1	128.4(3)
Pd–O1–C1	125.1(4)	C7–N1–Pd	123.5(2)

geometry about the Pd atom is seen to be approximately square planar, as defined by O1, N1 of the chelate and C14, C16 of the η^3-cyclohexenyl ligand. Very little geometric distortion of the Pd–allyl fragment relative to the Pd–chelate is apparent. Thus, the Pd–C14 and Pd–C16 bond lengths are identical (as are the Pd–O1 and Pd–N1 lengths) and the N1–Pd–C14 and O1–Pd–C16 angles (α) are nearly equal, indicating little or no difference in the trans influence of the N and O ends of the chelate. The most prominent difference between the structure of the oxazoline complex **7d** and the salicylaldimine derivative **5a** is the relationship between the α-N substituent and the flap of the cyclohexenyl ring—*exo* in the former and *endo* in the latter. This presumably reflects the combined steric effect of the bulky *tert*-butyl group and its positioning toward the coordinated cyclohexenyl unit by the rigid oxazoline ring of **7d** in comparison to the relatively free rotation about the N–C8 bond in salicylaldimine complex **5a**.

As another probe of the potentially unsymmetrical electronic character of the η^3-cyclohexenyl ligand of the isomeric oxazoline complexes **7** and the effect of aromatic ring substitution, we compare the chemical shifts of the allyl proton resonances of the singly isomeric *tert*-butyl derivatives in Table III. The terminal allylic proton resonances are seen to be well separated ($\delta(H_c) - \delta(H_b)$ = ca. 0.4–0.5 ppm), indicating significantly different electronic or magnetic environments. Assignment of the terminal $H_{b,c}$ resonances is based in part upon NOE experiments in which irradiation of the *tert*-butyl group was found to cause a greater enhancement of the higher field resonance, hence its assignment as H_b, cis to N. This assignment is consistent with the allylic proton chemical

Table III. ^{1}H NMR Data for the Allyl Fragment of *tert*-Butyloxazoline Complexes 7d,f,h,j

compd	R_1	R_2	$\delta(H_a)^a$	$\delta(H_b)^b$	$\delta(H_c)^c$	$\delta(H_c) - \delta(H_b)$
7j	MeO	H	5.58	4.54	4.99	0.45
7d	H	H	5.59	4.54	5.01	0.47
7f	NO_2	H	5.64	4.70	5.12	0.42
7h	NO_2	NO_2	5.64	4.79	5.22	0.43

[a] Internal allyl C–H. [b] Terminal allyl C–H *cis* to N. [c] Terminal allyl C–H *trans* to N.

shifts of the previously cited (N,O-chelate)Pd(η^3-allyl) complexes and with the larger expected shielding of H_b because of stronger electron donation from a trans O^- vs a neutral N-donor atom. However, shielding of H_b because of its proximity to the *tert*-butyl group may also contribute. The significantly different ^{13}C NMR terminal allylic resonances of *tert*-butyl derivative **7d**, at 74 ppm (C16, trans to N) and 70 ppm (C14, trans to O), established by ^{13}C–^{1}H HETCOR experiments, is a somewhat more reliable indicator of electronic asymmetry. Other features of the ^{1}H NMR data include (1) a steady downfield shift of the terminal allylic proton resonances, $H_{b,c}$, as the electron-withdrawing character of the aromatic ring increases (e.g. **7j,d,f,h**) but (2) little change of the chemical shift of central allyl–H, H_a, in this series and (3) virtually no change in $\Delta\delta(H_c-H_b)$, a potential measure of the electronic asymmetry within the allyl unit. Hence, these data suggest (but do not unambiguously establish) a significant difference in the electron densities of the termini of the allyl unit, with the carbon trans to N being more electron deficient. Electron-withdrawing substituents on the aromatic ring appear to affect both terminal allyl carbons approximately equally.

Acetolysis and Nucleophilic Reactions of Allyl Complexes 4, 5, and 7. The reactivity of these new allyl complexes was tested in acetic acid and toward representative nucleophiles in order to evaluate them as models for intermediates in catalytic allylic oxidation and substitution, respectively. When cinnamyl complex **4** was stirred in acetic acid at 20 °C for 12 h, four products were formed, as determined by GC–MS: the acetate addition products 1-phenyl-2-propenyl acetate (32%) and cinnamyl acetate (21%) and oxidation products cinnamaldehyde (44%) and phenyl vinyl ketone (3%), along with Pd metal. Cyclohexenyl complex **5** reacted completely in acetic acid after 12 h (20 °C), forming cyclohexenyl acetate (ca. 80%) along with a small amount (ca. 5%) of cyclohexenol. These experiments indicate that the (salicylaldimine)Pd(allyl) derivatives can give allylic oxidation products under appropriate conditions, but the poor regioselectivity (from acetolysis of **4**) and the presence of *endo*/*exo* isomers of **5** cause us to be pessimistic about the prospects for highly selective allylic oxidations proceeding via chiral (salicylaldimine)Pd(η^3-allyl) intermediates.

On the other hand, the oxazoline derivatives **7** generally proved disappointingly unreactive toward acetic acid at room temperature, the reactivity decreasing in the order **7d** (3 days) ≈ **7c** > **7a** (5 days) > **7b** (8 days) ≫ **7e,f** (no reaction). The reaction of **7a** in acetic acid produced Pd metal, a substantial amount of the free salicyloxazoline ligand, and only a small amount of cyclohexenyl acetate. The corresponding reactions of **7c,d** gave instead stoichiometric quantities of (salicyloxazoline)$_2$Pd derivatives and again only a small amount (<10%) of cyclohexenyl acetate. Reaction of **7b** with acetic acid produced a stoichiometric amount of the bis-chelate complex (salicyloxazoline)$_2$Pd and 1 equiv of cyclohexenyl acetate.

Given the modest reactivity of the oxazolinyl derivatives toward acetic acid, we wondered whether they would have higher reactivity under more potent nucleophilic conditions. Accordingly, complexes **7a,d,e,f** were treated with Bu_4NOAc in THF; at room temperature no significant reaction was detected after 48 h. Under similar conditions the same complexes were also found to be unreactive toward $NaCH(CO_2Me)_2$ in THF. It is thus clear that the oxazoline-based allyl complexes have limited reactivity toward nucleophiles known to attack many cationic and some neutral Pd–allyl complexes.

The limited and variable production of cyclohexenyl acetate from reactions of the (salicyloxazoline)Pd(cyclohexenyl) complexes with acetic acid suggests that these compounds may not be viable models for intermediates in Pd-catalyzed allylic acetoxylation. Indeed, unpublished experiments in our laboratory have shown that (salicyloxazoline)$_2$Pd complexes are precatalysts for allylic acetoxylation in HOAc at 20 °C.[32] Furthermore, the greater reactivity of **7a,d** toward HOAc compared to that toward nucleophilic R_4NOAc and $NaCH(CO_2Me)_2$ is consistent with an initial protonation pathway. The nonreactivity of the more electron-deficient (presumably less basic) nitro-substituted derivatives **7f,g** toward HOAc supports this hypothesis. Following protonation, acetate attack could give the allylic acetate or proton transfer to the cyclohexenyl ligand could produce cyclohexene.

Conclusions. Although our ultimate objective of producing effective chiral models for asymmetric allylic oxidation catalysts has not yet been met, a number of significant results relevant to this objective have been obtained. First, η^3-allyl derivatives of the chiral, unsymmetrical bidentate ligand *N*-(α-methylbenzyl)salicylaldimine have been prepared. The cyclohexenyl derivative **5** exists as two slowly interconverting isomers in solution, but one selectively crystallizes. X-ray diffraction of this isomer shows the phenyl group and the cyclohexenyl flap to be in an *endo* conformation with little evidence of a significantly different O vs N trans influence. Several sterically and electronically varied salicyloxazolines, a new class of chiral, N,O-bidentate ligands, have been prepared along with the corresponding series of Pd(η^3-cyclohexenyl) complexes. Solution NMR and X-ray crystallographic studies indicate that the ratio of solution rotamers can be controlled through the bulk of the α-N substituent, with single isomers present for R = *tert*-butyl. X-ray diffraction has shown the *tert*-butyl group and the cyclohexenyl flap of **7d** to be *exo* with little ground-state *trans* influence apparent. The ^{1}H and ^{13}C NMR spectra of **7**, on the other hand, are suggestive of an electronically unsymmetrical allyl unit, with moderate transmission of electronic effects from aromatic substituents. Unfortunately, the complexes **7** are rather unreactive and poorly chemoselective toward acetic acid, blocking our efforts to evaluate the ability of the chiral *N,O*-oxazolyl ligands to direct enantioselective addition to the coordinated allyl fragment.

It is clear from this study that further reactivity tuning is needed to produce a viable chiral catalyst system for asymmetric allylic oxidation. More electrophilic (less basic) bidentate chelates are presently under consideration for this purpose. Nonetheless, the capability of controlling the Pd–allyl rotameric equilibrium via manipulation of

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the 2-position substituent in the oxazoline ring demonstrates the potential for influencing more generally the binding stereochemistry of substrates at the metal center of such complexes. Therefore, the salicyloxazoline ligands described herein may yet hold considerable promise as chiral ligands in other asymmetric catalytic reactions, a potential which we hope to realize in future studies.

Experimental Section

General Methods and Materials. All organometallic compounds were prepared under a nitrogen atmosphere using standard Schlenk and vacuum-line techniques. Glassware was oven-dried at 120 °C overnight prior to use. Hexane, ether, THF, and toluene were distilled from sodium/benzophenone. NMR spectra were recorded on a Varian XL-300 FT-NMR spectrometer using $CDCl_3$ as the solvent unless otherwise noted; all values are given in δ units (J values are in Hz). IR spectra were recorded on a Bio-Rad FT-IR spectrometer; all values are given in cm^{-1}. Mass spectra were recorded on a VG ZAB-E or Kratos HRMS-25 mass spectrometer.

Ethyl 2-hydroxybenzimidate, ethyl 2-hydroxybenzimidate hydrochloride, and L-serine isopropyl ester hydrochloride were prepared according to literature procedures.[25] L-*tert*-Leucinol was prepared by the reduction of L-*tert*-butylleucine using $LiAlH_4$.[33] Bis(μ-chloro)bis(η^3-cyclohexenyl)dipalladium was prepared from 3-chlorocyclohexene.[30]

Preparation of (*R*)-*N*-(α-Methylbenzyl)salicylaldimine. A solution of salicylaldehyde (3.0 g, 24.6 mmol) and (*R*)-*N*-α-methylbenzylamine (3.0 g, 24.8 mmol) in 60 mL of benzene was heated at reflux for 2 h, during which time the water (ca. 0.5 mL) was removed azeotropically. The reaction mixture then was concentrated, and the residual oil was crystallized from absolute ethanol to yield greenish yellow crystals (5.17 g, 94%): mp 71–72 °C; IR (KBr pellet) 3450 br w, 1625 vs, 1577 s, 1494 vs, 1279 vs, 852 s, 768 vs, 702 vs; ^1H NMR 8.42 (s, 1H), 7.3–7.4 (m, 7H), 6.98 (d, J = 8.0, 1H), 6.82 (t, J = 7.4, 1H), 4.29 (q, J = 6.6, 1H), 1.64 (d, J = 6.6, 3H); MS (DIP) m/e 225 (M, 37%), 121 (62%), 105 (100%), 77 (18%). Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71. Found: C, 80.22; H, 7.00.

Preparation of 5-Substituted 2-(2′-Hydroxyphenyl)-2-oxazolines (3a–d). The following procedure for 5-phenyl-2-(2′-hydroxyphenyl)-2-oxazoline (**3a**) is typical. Ethyl 2-hydroxybenzimidate hydrochloride (1.46 g, 7.21 mmol) and (*R*)-(−)-2-phenylglycinol (0.988 g, 7.21 mmol) were dissolved in 80 mL of isopropyl alcohol and heated at reflux for 24 h. The isopropyl alcohol was removed *in vacuo*, and the residual oil was extracted by hot hexane twice. The hexane extracts were combined, concentrated, and further purified by chromatography (silica gel, benzene eluant) and recrystallization from hexane, affording white crystals (1.25 g, 73%): mp 33–34 °C; IR (KBr pellet) 1638 vs, 1489 s, 1364 s, 1254 s, 1071 s, 956 s, 757 vs, 679 s; ^1H NMR 7.71 (dd, J = 1.7, 7.8, 1H), 7.2–7.5 (m, 6H), 7.03 (d, J = 8.3, 1H), 6.91 (t, J = 7.6, 1H), 5.49 (dd, J = 8.3, 10.0, 1H), 4.80 (dd, J = 8.3, 8.5, 1H), 4.23 (dd, J = 8.5, 10.0, 1H); MS (DIP) m/e 239 (M, 100%), 209 (19%), 180 (26%), 148 (79%), 121 (60%), 91 (47%). Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48. Found: C, 75.27; H, 5.45.

5-((Isopropyloxy)carbonyl)-2-(2′-hydroxyphenyl)-2-oxazoline (3b, 80%): mp 32–33 °C; IR (KBr pellet) 2979 s, 1737 vs, 1639 vs, 1489 s, 1207 s, 756 s; ^1H NMR 7.68 (dd, J = 1.7, 7.9, 1H), 7.39 (m, 1H), 7.01 (d, J = 8.7, 1H), 6.89 (m, 1H), 5.10 (sept, J = 6.2, 1H), 4.92 (dd, J = 7.6, 10.0, 1H), 4.66 (dd, J = 7.6, 8.8, 1H), 4.57 (dd, J = 8.8, 10.0, 1H), 1.30 (d, J = 6.2, 6H); MS (DIP) m/e 249 (M, 22%), 207 (10%), 162 (100%), 134 (42%), 107 (36%). Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07. Found: C, 63.02; H, 6.16.

5-*sec*-Butyl-2-(2′-hydroxyphenyl)-2-oxazoline (3c, 64%): mp 27–28 °C; IR (KBr pellet) 2963 s, 1641 vs, 1490 s, 1365 s, 756 s; ^1H NMR 7.61 (dd, J = 1.5, 7.8, 1H), 7.36 (td, J = 7.8, 1.6, 1H), 7.00 (d, J = 8.3, 1H), 6.84 (t, J = 7.8, 1H), 4.40 (dd, J = 7.9, 9.3, 1H), 4.22 (m, 1H), 4.11 (t, J = 7.9, 1H), 1.6–1.7 (m, 2H), 1.2–1.3 (m, 1H), 0.92 (m, 3H), 0.88 (d, J = 6.7, 3H); MS (DIP) m/e 219 (M, 32%), 162 (100%), 134 (25%), 121 (15%), 107 (21%). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81. Found: C, 70.99; H, 7.64.

5-*tert*-Butyl-2-(2′-hydroxyphenyl)-2-oxazoline (3d, 70%): mp 27–28 °C; IR (KBr pellet) 2961 s, 1642 vs, 1490 s, 1363 s, 1259 s, 1075 s, 960 s, 763 s; ^1H NMR 7.62 (dd, J = 1.7, 7.8, 1H), 7.39 (m, 1H), 7.01 (d, J = 7.3, 1H), 6.89 (td, J = 7.3, 1.2, 1H), 5.38 (dd, J = 8.6, 10.0, 1H), 4.21 (dd, J = 7.8, 8.6, 1H), 4.12 (dd, J = 7.8, 10.0, 1H), 0.96 (s, 9H); MS (DIP) m/e 219 (M, 35%), 162 (100%), 134 (46%), 121 (21%), 107 (40%). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81. Found: C, 71.19; H, 7.89.

Preparation of 5-Substituted 2-(2′-Hydroxy-5′-nitrophenyl)-2-oxazolines and 5-Substituted 2-(2′-Hydroxy-3′,5′-dinitrophenyl)-2-oxazolines (3e–j). The following procedure for 5-phenyl-2-(2′-hydroxy-5′-nitrophenyl)-2-oxazoline (**3e**) is representative. To a suspension of 5-nitrosalicylic acid (267 mg, 1.46 mmol) in 5 mL of pyridine–acetonitrile (1:1) was added (R)-(−)-2-phenylglycinol (200 mg, 1.46 mmol), triethylamine (442 mg, 4.38 mmol), diisopropylethylamine (565 mg, 4.38 mmol), and carbon tetrachloride (2.70 g, 17.5 mmol) in that sequence. To this mixture was added a solution of triphenylphosphine (1.15 g, 4.38 mmol) in 8 mL of pyridine–acetonitrile (1:1) dropwise over a 1-h period. The reaction mixture was then stirred at room temperature for 24 h. The precipitate was removed by filtration and washed with benzene twice, and the combined filtrates were dried *in vacuo*. The residue was purified by silica gel chromatography, with benzene–acetic acid (100:1) as eluant. The crude product was further purified by recrystallization from ether–hexane to yield white crystals (278 mg, 67%): mp 100–101 °C; IR (KBr pellet) 3440 w, 3057 w, 1439 s, 1189 vs, 1120 vs, 754 s, 723 s, 698 vs, 541 vs; ^1H NMR 8.69 (d, J = 2.9, 1H), 8.31 (dd, J = 2.9, 9.1, 1H), 7.35–7.45 (m, 5H), 7.11 (d, J = 9.1, 1H), 5.53 (dd, J = 8.9, 10.1, 1H), 4.90 (dd, J = 8.7, 8.9, 1H), 4.36 (dd, J = 8.7, 10.1, 1H); MS (DIP) m/e 284 (M, 100%), 254 (18%), 193 (91%), 166 (55%), 132 (37%), 103 (25%), 91 (67%), 63 (21%). Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.38; H, 4.26; N, 9.85. Found: C, 63.53; H, 4.22; N, 9.86.

5-*tert*-Butyl-2-(2′-hydroxy-5′-nitrophenyl)-2-oxazoline: pale yellow crystals (**3f**, 44%); mp 49–50 °C; IR (KBr pellet) 1649 s, 1617 s, 1580 s, 1527 s, 1482 s, 1339 vs, 1227 s, 1123 s, 1056 s, 937 s, 841 s, 748 s, 640 s; ^1H NMR 8.60 (d, J = 2.8, 1H), 8.29 (dd, J = 2.8, 9.1, 1H), 7.10 (d, J = 9.1, 1H), 4.48 (dd, J = 8.9, 10.0, 1H), 4.32 (dd, J = 7.9, 8.9, 1H), 4.20 (dd, J = 7.9, 10.0, 1H), 0.95 (s, 9H); MS (DIP) m/e (M). Anal. Calcd for $C_{13}H_{16}N_2O_4$: C, 59.08; H, 6.10; N, 10.60. Found: C, 59.19; H, 5.99; N, 10.60.

5-Phenyl-2-(2′-hydroxy-3′,5′-dinitrophenyl)-2-oxazoline (3g, 38%): mp 204–205 °C; IR (KBr pellet) 1660 vs, 1554 vs, 1482 s, 1430 s, 1314 vs, 1255 s, 1081 s, 931 w, 760 s, 701 s; ^1H NMR 8.99 (d, J = 2.9, 1H), 8.84 (d, J = 2.9, 1H), 7.3–7.4 (m, 5H), 5.60 (dd, J = 8.7, 9.9, 1H), 5.10 (dd, J = 8.7, 8.9, 1H), 4.60 (dd, J = 8.9, 9.9, 1H); MS (DIP) m/e 329 (M, 100%), 299 (68%), 252 (31%), 238 (32%), 211 (46%), 119 (60%), 103 (35%), 91 (96%), 77 (40%). Anal. Calcd for $C_{15}H_{11}N_3O_6$: C, 54.72; H, 3.37. Found: C, 54.72; H, 3.48.

5-*tert*-Butyl-2-(2′-hydroxy-3′,5′-dinitrophenyl)-2-oxazoline (3h, 22%): mp 180–181 °C; IR (KBr pellet) 1644 vs, 1556 vs, 1436 s, 1360 s, 1309 vs, 1165 w, 1148 w, 1082 s, 930 s, 980 s, 746 w, 707 w; ^1H NMR 9.00 (d, J = 2.9, 1H), 8.78 (d, J = 2.9, 1H), 4.79 (dd, J = 8.9, 9.8, 1H), 4.61 (dd, J = 7.9, 8.9, 1H), 4.30 (dd, J = 7.9, 9.8, 1H), 1.02 (s, 9H); MS (DIP) m/e 309 (M, 13%), 235 (36%), 57 (100%). Anal. Calcd for $C_{13}H_{15}N_3O_6$: C, 50.49; H, 4.89; N, 13.59. Found: C, 50.12; H, 4.60; N, 13.49.

5-Phenyl-2-(2′-hydroxy-5′-methoxyphenyl)-2-oxazoline (3i, 27%): mp 122–123 °C; IR (KBr pellet) 1640 vs, 1594 vs, 1460 s, 1370 s, 1290 s, 1032 s, 958 vs, 835 s, 709 s, 642 w; ^1H NMR 7.2–7.4 (m, 2H), 6.94–7.13 (m, 1H), 5.48 (dd, J = 8.9, 10.0, 1H), 4.80 (dd, J = 8.3, 10.0, 1H), 4.21 (dd, J = 8.3, 8.9, 1H), 3.79 (s, 3H); MS (DIP) m/e 269 (M, 74%), 178 (43%), 149 (100%). Anal.

(33) Dickman, D. A.; Meyers, A. I. *Organic Syntheses*; Wiley: New York, 1990; Collect. Vol. VI, p 530.

Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.42; H, 5.53; N, 5.20.

5-*tert*-Butyl-2-(2′-hydroxy-5′-methoxyphenyl)-2-oxazoline (3j, 19%): oil; IR (KBr pellet) 1648 s, 1593 s, 1495 s, 1365 s, 1290 s, 1182 w, 1039 s, 933 w, 772 vs; ^{1}H NMR 7.10 (m, 1H), 6.9–7.0 (m, 2H), 4.33 (dd, J = 8.6, 10.0, 1H), 4.20 (dd, J = 7.8, 8.6, 1H), 4.10 (dd, J = 7.8, 10.0, 1H), 3.77 (s, 3H), 0.93 (s, 9H); MS (DIP) m/e 249 (M, 48%), 192 (100%), 164 (30%), 150 (26%), 149 (52%).

Preparation of [(*R*)-*N*-(α-Methylbenzyl)salicylaldimine]-[η³-cyclohexenyl]palladium (5). To a solution of (*R*)-*N*-(α-methylbenzyl)salicylaldimine (150 mg, 0.67 mmol) in toluene (10 mL) was added a 1.0 M solution (0.7 mL) of potassium *tert*-butoxide in THF. A solution of bis(μ-chloro)bis(η³-cyclohexenyl)-dipalladium (149 mg, 0.33 mmol) in toluene (30 mL) was added dropwise at 0 °C over 30 min to this mixture. The mixture was stirred for an additional 6 h while the solution was warmed gradually to room temperature. After the precipitate was removed by centrifugation, the yellow solution was concentrated to about 5 mL and hexane was added. Greenish yellow crystals (238 mg, 87%) separated after keeping the solution in the freezer (−20 °C) overnight: IR (KBr pellet) 1607 vs, 1503 s, 1465 s, 1446 vs, 1414 s, 1353 s, 1187 s, 773 s, 756 s; ^{1}H NMR 8.26 (s, 1H), 8.17 (s, 1H), 7.36 (m, 10H), 7.16 (dd, J = 1.8, 7.8, 1H), 7.10 (dd, J = 1.8, 7.8, 1H), 6.96 (d, J = 8.3, 2H), 6.52 (q, J = 6.8, 2H), 5.47 (t, J = 6.5, 1H), 5.37 (t, J = 6.5, 1H), 5.09 (m, 1H), 4.9–5.0 (m, 3H), 4.22 (t, J = 6.3, 1H), 3.92 (t, J = 6.3, 1H), 1.78 (d, J = 6.8, 3H), 1.74 (d, J = 6.8, 3H), 0.5–1.7 (m, 12H); MS (FAB) m/e (M). Anal. Calcd for $C_{21}H_{23}NOPd$: C, 61.24; H, 5.63. Found: C, 60.84; H, 5.95.

Preparation of [5-Substituted 2-(2′-phenolato)oxazolyl], [5-Substituted 2-(5′-nitro-2′-phenolato)oxazolyl]-, [5-Substituted 2-(3′,5′-dinitro-2′-phenolato)oxazolyl]-, and [5-Substituted 2-(5′-methoxy-2′-phenolato)oxazolyl][η³-cyclohexenyl]palladium Complexes (7a–j). The following procedure for the preparation of [5-phenyl-2-(2′-phenolato)-2-oxazolyl][η³-cyclohexenyl]palladium (**7a**) is representative. To a solution of 5-phenyl-2-(2′-hydroxyphenyl)-2-oxazoline (224 mg, 0.94 mmol) and bis(μ-chloro)bis(η³-cyclohexenyl)dipalladium (209 mg, 0.47 mmol) in 50 mL of toluene was added a solution of potassium (37 mg, 0.95 mmol) in *tert*-butyl alcohol (1.2 mL). The solution was stirred at room temperature for 18 h, and the precipitate was removed by centrifugation. The solution was then concentrated to ca. 8 mL, and hexane was added. A pale yellow solid (310 mg, 78%) separated after keeping the solution in the freezer (−20 °C) overnight: IR (KBr pellet) 1616 vs, 1531 s, 1468 s, 1443 vs, 1259 vs, 1155 s, 1071 s, 850 s, 753 vs; ^{1}H NMR 7.70 (m, 1H), 7.2–7.4 (m, 6H), 6.91 (m, 1H), 6.45 (m, 1H), 5.30–5.47 (m, 2H), 5.10 (t, J = 6.4, 1H), 4.65–4.80 (m, 2H), 4.18 (m, 1H), 0.7–1.9 (m, 6H); MS (FAB) m/e 425 (M, 40%), 345 (42%), 240 (44%), 147 (100%), 136 (62%). Anal. Calcd for $C_{21}H_{21}NO_2Pd$: C, 59.23; H, 4.97. Found: C, 59.54; H, 5.75.

[5-((Isopropyloxy)carbonyl)-2-(2′-phenolato)-2-oxazolyl]-[η³-cyclohexenyl]palladium (7b): pale yellow solid (65%); IR (KBr pellet) 1737 s, 1616 s, 1492 w, 1372 w, 1106 s, 963 w, 850 vs; ^{1}H NMR 7.66 (m, 1H), 7.2–7.3 (m, 1H), 6.92 (d, J = 8.7, 1H), 6.46 (t, J = 7.5, 1H), 5.52 (m, 1H), 4.8–5.2 (m, 3H), 4.4–4.7 (m, 3H), 1.5–2.0 (m, 5H), 1.0–1.1 (m, 1H); MS (FAB) m/e 435 (M, 77%), 355 (67%), 312 (62%), 250 (74%), 208 (100%), 185 (32%), 162 (49%).

[5-*sec*-Butyl-2-(2′-phenolato)-2-oxazolyl][η³-cyclohexenyl]-palladium (7c): pale yellow solid (72%); IR (KBr pellet) 1620 vs, 1534 s, 1467 vs, 1441 s, 1389 s, 1351 s, 1229 vs, 1063 s, 752 s; ^{1}H NMR major isomer (60%), 7.65 (dd, J = 1.9, 8.1, 1H), 7.24 (m, 1H), 6.93 (dd, J = 1.1, 8.7, 1H), 6.47 (m, 1H), 5.64 (t, J = 6.4, 1H), 5.14 (m, 1H), 4.56 (t, 1H), 4.2–4.4 (m, 3H), 1.6–2.1 (m, 6H), 1.2–1.4 (m, 3H), 1.0–1.1 (m, 3H), 0.70 (d, J = 6.9, 3H); ^{1}H NMR minor isomer (40%), 7.64 (dd, J = 1.9, 8.1, 1H), 7.24 (m, 1H), 6.92 (dd, J = 1.1, 8.7, 1H), 6.47 (m, 1H), 5.58 (t, J = 6.6, 1H), 5.01 (m, 1H), 4.50 (t, 1H), 4.2–4.4 (m, 3H), 1.6–2.1 (m, 6H), 1.2–1.4 (m, 3H), 1.0–1.1 (m, 3H), 0.82 (d, J = 6.8, 3H); MS (FAB) m/e 405 (M, 95%), 325 (48%), 220 (100%). Anal. Calcd for $C_{19}H_{25}NO_2Pd$: C, 56.23; H, 6.21. Found: C, 55.82; H, 6.20.

[5-*tert*-Butyl-2-(2′-phenolato)-2-oxazolyl][η³-cyclohexenyl]palladium (7d): yellow crystals (68%); IR (KBr pellet) 1612 vs, 1533 vs, 1466 s, 1442 vs, 1383 vs, 1353 vs, 1266 s, 1230 vs, 929 s, 760 vs; ^{1}H NMR 7.66 (dd, J = 1.9, 8.6, 1H), 7.25 (dd, J = 1.9, 6.7, 1H), 6.92 (dd, J = 1.1, 8.6, 1H), 6.45 (m, 1H), 5.59 (t, J = 6.3, 1H), 5.01 (t, J = 6.3, 1H), 4.54 (t, J = 6.3, 1H), 4.49 (dd, J = 3.0, 8.9, 1H), 4.31 (t, J = 8.9, 1H), 3.95 (dd, J = 3.0, 8.9, 1H), 1.6–2.0 (m, 6H), 0.95 (s, 9H); MS (FAB) m/e 405 (M, 75%), 324 (54%), 220 (100%), 162 (29%). Anal. Calcd for $C_{19}H_{25}NO_2Pd$: C, 56.23; H, 6.21. Found: C, 56.20; H, 6.35.

[5-Phenyl-2-(5′-nitro-2′-phenolato)-2-oxazolyl][η³-cyclohexenyl]palladium (7e): yellow crystals (66%); IR (KBr pellet) 1621 vs, 1549 s, 1489 s, 1455 s, 1360 s, 131 vs, 1265 s, 1121 s, 835 s, 711 s; ^{1}H NMR 8.82 (t, J = 3.0, 1H), 8.11 (dd, J = 3.0, 9.6, 1H), 7.3–7.5 (m, 5H), 6.85 (dd, J = 1.4, 9.6, 1H), 5.35–5.55 (m, 2H), 5.10–5.25 (m, 1H), 4.79–4.92 (m, 2H), 4.25–4.35 (m, 1H), 0.8–2.0 (m, 6H); MS (FAB) m/e 470 (M, 100%), 454 (14%), 389 (23%), 375 (17%), 285 (79%). Anal. Calcd for $C_{21}H_{20}N_2O_4Pd$: C, 53.57; H, 4.28; N, 5.95. Found: C, 53.51; H, 4.20; N, 5.82.

[5-*tert*-Butyl-2-(5′-nitro-2′-phenolato)-2-oxazolyl][η³-cyclohexenyl]palladium (7f): yellow crystals (89%); IR (KBr pellet) 1621 vs, 1547 s, 1485 vs, 1433 s, 1319 vs, 1280 vs, 1229 s, 1123 vs, 1055 s, 978 s, 835 s, 713 s; ^{1}H NMR 8.73 (d, J = 3.0, 1H), 8.10 (dd, J = 3.0, 9.5, 1H), 6.80 (d, J = 9.5, 1H), 5.64 (t, J = 6.1, 1H), 5.12 (t, J = 6.1, 1H), 4.70 (t, J = 6.1, 1H), 4.58 (dd, J = 3.2, 9.0, 1H), 4.39 (t, J = 9.0, 1H), 3.99 (dd, J = 3.2, 9.0, 1H), 1.6–2.0 (m, 6H), 0.95 (s, 9H); MS (FAB) m/e 450 (M, 47%), 265 (100%). Anal. Calcd for $C_{19}H_{24}N_2O_4Pd$: C, 50.62; H, 5.37; N, 6.21. Found: C, 50.85; H, 5.53; N, 6.19.

[5-Phenyl-2-(3′,5′-dinitro-2′-phenolato)-2-oxazolyl][η³-cyclohexenyl]palladium (7g): yellow crystals (72%); IR (KBr pellet) 1629 vs, 1354 s, 1254 s, 1144 s, 704 s, 699 s; ^{1}H NMR 8.91 (t, J = 3.0, 1H), 8.78 (d, J = 3.0, 1H), 7.3–7.5 (m, 5H), 5.35–5.50 (m, 2H), 5.20 (m, 1H), 4.80–4.95 (m, 2H), 4.25–4.35 (m, 1H), 0.7–1.9 (m, 6H); MS (FAB) m/e 516 (M + 1, 100%), 330 (56%), 273 (30%), 169 (26%), 147 (51%), 128 (44%), 104 (46%). Anal. Calcd for $C_{21}H_{19}N_3O_6Pd$: C, 48.90; H, 3.71; N, 8.15. Found: C, 48.64; H, 3.75; N, 8.29.

[5-*tert*-Butyl-2-(3′,5′-dinitro-2′-phenolato)-2-oxazolyl][η³-cyclohexenyl]palladium (7h): yellow crystals (34%); IR (KBr pellet) 1627 vs, 1533 s, 1320 vs, 1247 s, 1153 s, 721 vs, 708 s; ^{1}H NMR 8.83 (d, J = 3.0, 1H), 8.76 (d, J = 3.0, 1H), 5.64 (t, J = 6.1, 1H), 5.22 (t, J = 6.1, 1H), 4.79 (t, J = 6.1, 1H), 4.57 (dd, J = 3.2, 9.0, 1H), 4.40 (t, J = 9.0, 1H), 4.00 (dd, J = 3.2, 9.0, 1H), 1.6–1.9 (m, 6H), 0.96 (s, 9H); MS (FAB) m/e 496 (M + 1, 100%), 415 (22%), 310 (40%), 187 (24%).

[5-Phenyl-2-(5′-methoxy-2′-phenolato)-2-oxazolyl][η³-cyclohexenyl]palladium (7i): yellow crystals (75%); IR (KBr pellet, cm^{-1}) 1640 vs, 1493 s, 1460 s, 1370 s, 958 vs, 835 vs, 607 s; ^{1}H NMR 7.15–7.40 (m, 2H), 6.9–7.0 (m, 1H), 5.31–5.50 (m, 2H), 5.10–5.20 (m, 1H), 4.69–4.81 (m, 2H), 4.15–4.25 (m, 1H), 3.74 (two s, 3H), 0.8–2.0 (m, 6H); MS (FAB) m/e 456 (M, 100%), 375 (40%), 271 (26%).

[5-*tert*-Butyl-2-(5′-methoxy-2′-phenolato)-2-oxazolyl][η³-cyclohexenyl]palladium (7j): yellow crystals (70%); IR (KBr pellet, cm^{-1}) 1648 s, 1495 s, 1366 s, 1290 vs, 1039 s, 772 vs; ^{1}H NMR 7.10 (m, 1H), 6.80–7.0 (m, 2H), 5.58 (t, J = 6.3, 1H), 4.99 (t, J = 6.3, 1H), 4.54 (t, J = 6.3, 1H), 4.48 (dd, J = 2.6, 9.0, 1H), 4.29 (t, J = 9.0, 1H), 3.93 (dd, J = 2.6, 9.0, 1H), 3.72 (s, 3H), 1.6–2.0 (m, 6H), 0.90 (s, 9H); MS (FAB) m/e 435 (M, 3%), 261 (21%), 250 (80%), 249 (100%), 192 (12%).

Acetolysis of 4, 5, and 7. A solution of **4**, **5**, or **7a–f** (10 mg) in 2 mL of acetic acid was stirred at room temperature until the completion of decomposition, as evidenced by precipitation of palladium black. The latter was separated by centrifugation. The acetic acid solution was poured into 10 mL of water and extracted with hexane three times. The combined hexane extracts were evaporated at 20 mm. From cinnamyl complex **4** the following products were detected by GC–MS: 1-phenyl-2-propenyl acetate (32%), cinnamyl acetate (21%), cinnamaldehyde

Table IV. Crystal Data for 5 and 7d

	5	7d
formula	$C_{21}H_{22}NOPd \cdot 0.5C_9H_{20}$	$C_{19}H_{25}NOPd$
fw	474.94	405.25
temp, K	160	160
a, Å	9.112(2)	11.074(3)
b, Å	10.021(3)	15.596(4)
c, Å	22.926(5)	10.195(3)
β, deg	98.48(4)	
V, Å^3	2072.1	1760.8
space group	$P2_1$	$P2_12_12_1$
Z	4	4
density, g/cm^3	1.522	1.531
μ(Mo Kα), cm^{-1}	8.4	9.8
F(000)	984	832
data collecn range, 2θ, deg	1.5–53	1.5–54
total no. of rflns measd	4475	2210
no. of rflns used ($I > 2\sigma(I)$)	3379	1987
R^a	0.068	0.019
R_w^b	0.094	0.025
GOF^c	3.6	1.1
largest shift/esd, final cycle	0.8	0.1
ρ_{max} final diff map, e/Å^3	2.1	0.36

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. ^{c} GOF $= [\sum w|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

Table V. Atomic Coordinates for 5 (Molecule 1)

atom	x	y	z
Pd1	0.95590(9)	–0.50000	0.89393(4)
O1	1.0105(9)	–0.3215(9)	0.8572(4)
N1	0.7306(10)	–0.4510(10)	0.8752(4)
C1	0.9206(15)	–0.2236(15)	0.8372(7)
C2	0.9843(14)	–0.1022(12)	0.8205(5)
C3	0.8835(14)	0.0018(13)	0.7976(5)
C4	0.7528(18)	–0.0024(16)	0.7930(6)
C5	0.6772(14)	–0.1209(13)	0.8069(6)
C6	0.7682(13)	–0.2314(13)	0.8305(6)
C7	0.6815(18)	–0.3394(23)	0.8483(8)
C8	0.6088(12)	–0.5471(11)	0.8888(5)
C9	0.6131(17)	–0.6747(14)	0.8525(6)
C10	0.6233(12)	–0.5650(14)	0.9556(5)
C11	0.6603(14)	–0.4560(13)	0.9926(6)
C12	0.6620(15)	–0.4621(12)	1.0548(6)
C13	0.6320(13)	–0.5814(14)	1.0802(6)
C14	0.5990(14)	–0.6913(13)	1.0424(6)
C15	0.5950(13)	–0.6797(13)	0.9807(5)
C16	0.9710(15)	–0.6790(15)	0.9479(6)
C17	1.0859(14)	–0.6722(13)	0.9125(6)
C18	1.1799(12)	–0.5651(14)	0.9212(6)
C19	1.2309(14)	–0.5144(18)	0.9844(7)
C20	1.1313(22)	–0.5564(20)	1.0293(8)
C21	1.0028(14)	–0.6335(17)	1.0122(6)

(44%), and phenyl vinyl ketone (3%), along with Pd metal. Cyclohexenyl complex **5** reacted completely after 12 h, forming cyclohexenyl acetate (ca. 80%) along with a small amount (ca. 5%) of cyclohexenol. The reactivity of **7** was found to decrease in the order **7d** (3 days) ≈ **7c** > **7a** (5 days) > **7b** (8 days) ≫ **7e,f** (no reaction). The reaction of **7a** produced Pd metal, a substantial amount of the free salicyloxazoline ligand, and only a small amount of cyclohexenyl acetate. The reactions of **7c,d** gave stoichiometric quantities of (salicyloxazoline)$_2$Pd derivatives and only a small amount (<10%) of cyclohexenyl acetate. Reaction of **7b** with acetic acid produced a stoichiometric amount of (salicyloxazoline)$_2$Pd and 1 equiv of cyclohexenyl acetate.

Reaction of 7. (1). With LiOAc or Bu$_4$NOAc. Tetrabutylammonium acetate (0.03 mmol) was added to a solution of **7a** or **7e** (0.03 mmol) in THF (1 mL). This solution was stirred at room temperature for 24–48 h, during which time only slight decomposition of the complex was observed.

(2). With Sodium Dimethylmalonate. **7a** or **7e** (0.03 mmol) was dissolved in a THF solution containing 3 equiv of sodium dimethylmalonate (prepared by treatment of dimethyl malonate with NaH in THF). This solution was stirred at room temperature for 12–24 h, during which time only slight decomposition (palladium deposition) of the complex was observed.

Table VI. Atomic Coordinates for 5 (Molecule 2)

atom	x	y	z
Pd1A	0.54478(11)	0.02143(10)	0.60661(5)
O1A	0.4959(10)	0.2020(10)	0.6461(5)
N1A	0.7760(11)	0.0660(12)	0.6282(5)
C1A	0.5852(14)	0.2958(14)	0.6654(6)
C2A	0.5312(15)	0.4201(14)	0.6808(6)
C3A	0.6030(18)	0.5224(16)	0.7019(7)
C4A	0.7745(13)	0.5153(13)	0.7139(6)
C5A	0.8351(15)	0.3932(14)	0.6960(7)
C6A	0.7517(14)	0.2841(13)	0.6726(6)
C7A	0.8282(14)	0.1695(13)	0.6536(6)
C8A	0.8857(13)	–0.0251(16)	0.6115(6)
C9A	0.8802(16)	–0.1595(14)	0.6449(6)
C10A	0.8729(12)	–0.0440(14)	0.5431(6)
C11A	0.8974(15)	–0.1607(13)	0.5166(7)
C12A	0.9018(16)	–0.1671(15)	0.4545(7)
C13A	0.8697(15)	–0.0512(17)	0.4213(7)
C(14A)	0.8422(15)	0.0651(16)	0.4479(7)
C15A	0.8356(15)	0.0713(15)	0.5095(17)
C16A	0.5309(18)	–0.1531(15)	0.5510(8)
C17A	0.4162(16)	–0.1472(14)	0.5878(8)
C18A	0.3142(14)	–0.0341(16)	0.5788(7)
C19A	0.2778(14)	0.0252(14)	0.5168(6)
C20A	0.3385(21)	–0.0435(21)	0.4713(9)
C21A	0.4910(20)	–0.1013(20)	0.4861(8)

Table VII. Atomic Coordinates for 7d

atom	x	y	z
Pd1	0.00585(2)	0.09608(1)	0.22810(2)
O1	0.1106(2)	0.1789(1)	0.3413(3)
O2	0.3438(2)	0.0860(1)	0.0381(2)
N1	0.1497(2)	0.0905(2)	0.0975(2)
C1	0.2284(2)	0.1762(2)	0.3476(3)
C2	0.2848(3)	0.2122(2)	0.4608(3)
C3	0.4076(3)	0.2079(2)	0.4801(4)
C4	0.4823(3)	0.1681(2)	0.3884(3)
C5	0.4324(2)	0.1348(2)	0.2765(3)
C6	0.3061(2)	0.1389(2)	0.2537(3)
C7	0.2607(2)	0.1050(2)	0.1310(3)
C8	0.2802(3)	0.0397(2)	–0.0642(4)
C9	0.1481(3)	0.0642(2)	–0.0420(3)
C10	0.1010(3)	0.1370(2)	–0.1339(3)
C11	0.1829(3)	0.2160(2)	–0.1270(4)
C12	–0.0269(4)	0.1625(3)	–0.0937(5)
C13	0.0989(4)	0.1024(3)	–0.2735(4)
C14	–0.1111(3)	–0.0014(2)	0.1595(4)
C15	0.1770(3)	0.0626(2)	0.2248(4)
C16	–0.1442(3)	0.0773(2)	0.3561(4)
C17	–0.1064(3)	0.0027(3)	0.4417(4)
C18	–0.1229(4)	–0.0828(3)	0.3729(5)
C19	–0.0765(3)	–0.0825(2)	0.2312(4)

X-ray Diffraction Studies of 5 and 7d. The crystal data for both compounds were measured on an Enraf-Nonius CAD-4 diffractometer using monochromated Mo Kα radiation (λ = 0.710 69 Å). The data were corrected for Lorentz and polarization effects. No absorption correction was applied, since it was judged to be insignificant for both crystals. The atomic scattering factors were taken from ref 34, and the structures were solved and refined by full-matrix least-squares methods (SHELX 86 and SHELX 76). See Table IV for details of the data collection and refinement.

For **5** the molecular refinement was poor due to the presence of a disordered solvent molecule in the asymmetric unit and pseudosymmetry. There are two independent molecules in the asymmetric unit, but they are closely related by an inversion center. For crystallization hexanes–toluene was used, but the former may contain higher hydrocarbons as well. Because of the disorder, the geometry of the solvent molecule is very poor; however, the difference map clearly shows nine peaks, which fits more closely to a nonane than to a hexane. For **5** all the non-hydrogen atoms of the Pd complex were refined anisotropically, the atoms of the solvent were refined isotropically, and hydrogen

(34) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974.

atoms were added in the idealized positions for the phenyl groups and at C8. Because of the difficulties in refinement, the final R factor is rather high and the final difference map shows two large peaks close to the Pd atom.

The refinement of **7d** proceeded smoothly. All the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were located and refined isotropically. Final crystal data are given in Table IV.

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Supplementary Material Available: Tables containing atomic coordinates for **5** (disordered solvent), hydrogen atom coordinates for **5** and **7d**, anisotropic thermal parameters for **5** and **7d**, and all bond angles and lengths for **5** and **7d** (17 pages). Ordering information is given on any current masthead page.

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