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Oxime-Based Salen-Type Tetradentate Ligands with High Stability against Imine Metathesis Reaction

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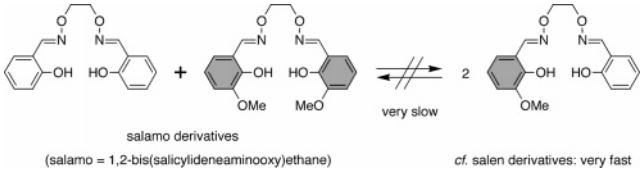

Although salen and its analogues are versatile chelate ligands in inorganic and organometallic chemistry, synthesis of unsymmetrical salen derivatives consisting of two different salicylideneimine moieties is difficult because of the C=N bond recombination. To develop stable analogues of salen-type ligands, we synthesized a series of new ligands salamo (=1,2-bis(salicylideneaminooxy)ethane) on the basis of *O*-alkyl oxime instead of the imine moiety. Eight salamo ligands **1a**−**h** were prepared in 64−88% yields as colorless crystals from the corresponding salicylaldehydes **2a**−**h**. The crystal structure of **1a**−**c** suggests that the oxime-OH form is more predominant than the keto-NH form. The reaction of **2a**−**e** with excess 1,2-bis(aminooxy)ethane gave monooximes **3a**−**e** in 59−86%, which further reacted with a different salicylaldehyde to afford unsymmetrical salamo ligands **4**−**8** as stable crystals in 51−70%. No reaction took place when a mixture of salamo derivatives **1a** and **1b** was treated at 40 °C in H_2O/MeCN (5:95). However, the metathesis reaction of salen derivatives **9a** and **9b** completed in 2 h to give a statistical mixture. Monooxime **3b** was much more stable than monoimine **11** which is difficult to be isolated. These results indicate the extremely high stability of the salamo derivatives **1** and precursors **3**.

Introduction

Salen (*N,N′*-disalicylideneethylenediamine) and its analogues are most versatile chelate ligands in inorganic and organometallic chemistry. Some of the metal complexes are used as a catalyst in various organic reactions,[1] nonlinear optical materials,[2] and metallomesogens[3] or exhibit interesting magnetic properties[4] and so forth. Although most of the metal complexes containing salen ligands are stable in solution and in the solid state, C=N bonds often suffer exchange reaction[5] as well as hydrolysis.[6] Such reversible C=N bond formation[7] is sometimes useful to synthesize the most thermodynamically stable macrocyclic[8] and interlocked compounds[9] in high yields. The labile nature of the C=N bonds is also successfully utilized to generate a dynamic combinatorial library.[10] However, such reversibility of the C=N bond

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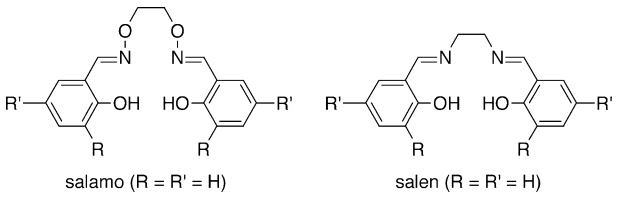
formation results in unfavorable ring contraction in the metalation process of some cyclic salen derivatives.[11,12] In some cases, macrocyclic imine is formed via C=N bond recombination of an acyclic diamine.[13]

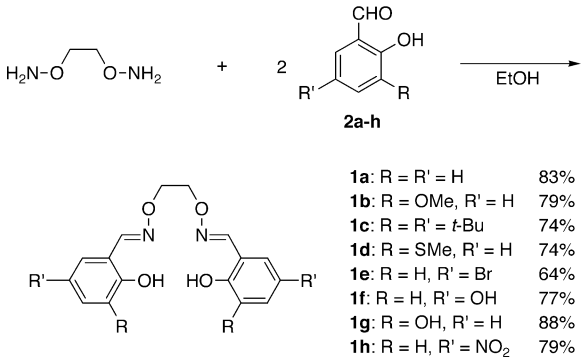
Synthesizing unsymmetrical salen derivatives, which consist of two different salicylideneimine moieties, is difficult because a statistical mixture of three possible condensation products is usually obtained.[14] Selective synthesis of these unsymmetrical ligands is important because electronic and steric effects of the ligands on salen-metal-assisted catalysis may be controlled by introduction of different substituents into the two benzene rings. In early works, metal complexes of unsymmetrical salen and analogues were prepared via the monoimine complexes without isolation of the unsymmetrical free ligands.[15,16] Recently, chiral unsymmetrical salen polymer complexes which are obtained from a statistical mixture of symmetrical and unsymmetrical ligands have been utilized for asymmetric catalysis.[17] The unsymmetrical salen derivatives can be also synthesized by stepwise condensation. In some cases, however, isolation of the intermediary monoimine as hydrochloride or (+)-*O*,*O*′-dibenzoyl-D-tartarates is necessary to obtain the unsymmetrical salens.[18] The unsymmetrical ligands thus obtained are sometimes contaminated by a small amount of symmetrical ligands because of unavoidable disproportionation.[14,18a]

Rate constants of oxime formation are smaller than those of imine formation and the equilibrium constants are larger by several orders.[19] Hence, the oxime-type ligands should be stable enough to resist the metathesis of the C=N bonds. Thus, we planned synthesis of a new salen-type chelate ligand salamo (=1,2-bis(salicylideneaminooxy)ethane) on the basis of *O*-alkyl oxime instead of the imine moiety (Chart 1). Linear derivatives bearing two salicylaldoxime moieties at both ends have been reported.[20] A cyclic ligand with a salamo moiety is isolated as mono- or binuclear complexes.[21] However, the intrinsic properties of salamo have been described only

CHART 1



SCHEME 1. Synthesis of Salamo Ligands 1



in our preliminary study.[22] In this paper, we report details of the synthesis and structure of the oxime-type chelate ligands and their stability against exchange reaction of the C=N bonds, compared with the corresponding salen derivatives. Unsymmetrical salamo derivatives are effectively synthesized because of their stability.

Results and Discussion

Synthesis and Characterization of Symmetrical Salamo Ligands. The oxime ligands **1** were synthesized according to the procedures shown in Scheme 1. Reaction of 1,2-bis(aminooxy)ethane[23] with 2 equivalents of salicylaldehyde derivatives **2** in ethanol afforded the desired chelates **1a**−**h** as colorless crystals in 64−88% yields. The products were easily obtained in pure form by filtering the precipitates from the reaction mixture or recrystallization.

In the ^{1}H NMR spectra of **1a**−**h**, singlets of methylene protons and oxime protons were observed at 4.3−4.5 and 8.1−8.4 ppm, respectively, showing the symmetrical structure of **1** (Table 1). The OH resonance at 9−11 ppm strongly suggests intramolecular hydrogen bonds between the oxime nitrogen and the phenolic hydroxyl groups. In the ^{13}C NMR spectra of **1**, the signals of the C=N carbon atoms were observed at 144−153 ppm. The IR spectra clearly indicate the C=N group because C=N stretching absorption bands of the ligands were observed at 1599−1627 cm^{-1}. The electronic absorption spectra shows $\pi-\pi^*$ bands at 303−339 nm. Although the corresponding salen analogues show a band around 400 nm assigned to their keto-NH form and the $\pi-\pi^*$ bands (ca. 315 nm),[24] **1** showed no absorption around 400 nm. This fact indicates that the population of the keto-NH form of salamo is negligibly small (Scheme 2).

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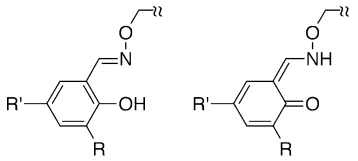
TABLE 1. Spectroscopic Data for Salamo Ligands 1

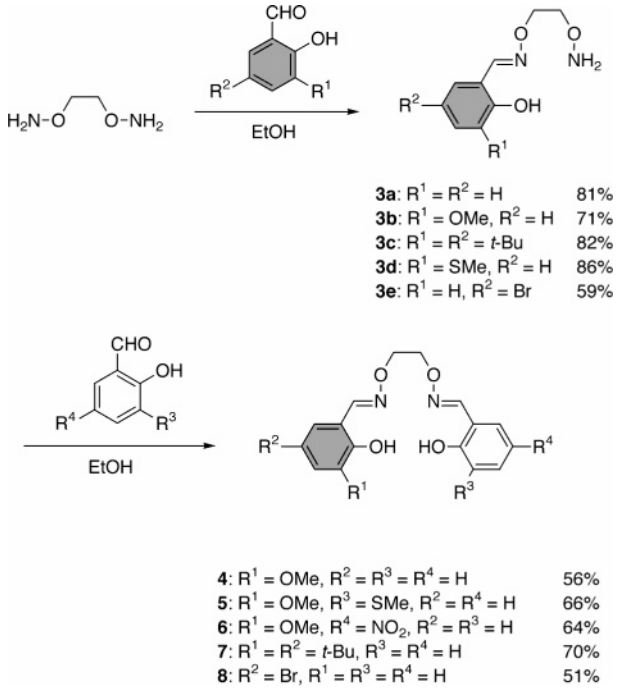
compound	δ_H (CH_2)[a]	δ_H (CH=N)[a]	δ_H (OH)[a]	δ_C (CH=N)[a]	ν(C=N)[b]	$\lambda(\pi-\pi^*)$[c]
1a	4.49	8.25	9.75	152.3	1608	310
1b	4.49	8.26	9.74	152.0	1605	316
1c	4.48	8.26	10.15	153.4	1612	321
1d	4.47	8.24	10.35	151.9	1599	327
1e	4.48	8.14	9.74	151.0	1613	323
1f	4.33[d]	8.31[d]	9.02, 9.34[d]	147.3[d]	1609	339
1g	4.50	8.22	5.56, 9.89	152.1	1626	317
1h	4.43[d]	8.36[d]	[e]	144.7[d]	1627	303

[a] In $CDCl_3$. [b] KBr. [c] In MeOH (2×10^{-5} M). [d] In DMSO-d_6. [e] The OH signal was not observed.

SCHEME 2



SCHEME 3. Synthesis of Unsymmetrical Salamo Ligands 4−8



Synthesis of Unsymmetrical Salamo Ligands via Monooxime. To synthesize the unsymmetrical salamo derivatives, stepwise introduction of the salicylidene moieties at both ends of 1,2-bis(aminooxy)ethane is effective (Scheme 3). Thus, we prepared the intermediates, monooximes **3**. The reaction of salicylaldehydes with excess 1,2-bis(aminooxy)ethane gave a mixture containing the desired monooximes **3** and a small amount of dioximes **1**. The pure monooximes **3a**−**e** were obtained in 59−86% yields after silica gel chromatographic separation of the crude product. The monooximes **3** were obtained as stable crystals or an oil. The reaction of salicylaldehydes with diamines is also reported to give the corresponding monoimine derivatives. Whereas the monoimine derivatives obtained from phenylenediamine are isolable,[14] aliphatic analogues containing ethylenediamine or cyclohexanediamine are generally unstable and cannot be isolated.[15]

By using the stable monooximes **3**, we can obtain unsymmetrical salamo ligands **4**−**8** bearing two different salicylaldoxime moieties. The reaction of the monooximes **3** with appropriate salicylaldehyde in ethanol afforded the unsymmetrical salamo derivatives **4**−**8** as colorless crystals in 51−70% yields. The compounds are sufficiently stable in solution as well as in the solid state. This method has been also applied to the synthesis of a linear bis(salamo) ligand containing two unsymmetrically substituted salamo chelate moieties.[25]

On the other hand, the corresponding unsymmetrical salen ligands can be obtained after chromatographic separation of the mixture containing symmetrical and unsymmetrical ligands.[15] Recently, more rational methods for the reaction have been reported.[18] Intermediate monoimine was isolated as hydrochlorides or (+)-*O*,*O*′-dibenzoyl-D-tartarates, which are further allowed to react with aldehydes to afford unsymmetrical salen ligands. However, this method is effective only when the monoimine forms a crystalline salt. Although the aromatic analogues of the monoimine derivatives are much more stable and can be isolated in high yield, a mixture of the three possible condensation products is obtained in the unsymmetrical saloph derivatives.[14] This is probably due to the exchange of the C=N bonds to cause redistribution of the aldehyde units of the unsymmetrical ligands.

We established a general synthetic method for unsymmetrical salamo ligands involving stepwise introduction of two different aldehyde units. Effectiveness of the method is mainly owing to the stability of the intermediate monooximes **3**, which can be easily isolated. In addition, greater stability of the unsymmetrical salamo derivatives **4**−**8** than that of the imine analogues (vide infra) also contributes to the higher yields.

Structure of Salamo Ligands. X-ray crystallographic analysis revealed the crystal structure of the oxime chelate ligands **1a**, **1b**, **1c**, and **4**. A noticeable conformational difference was observed in the N−O−CH_2−CH_2−O−N linkage between two salicylidene moieties of the four molecules, whereas geometries of the salicylaldoxime moieties are similar.

Parent salamo **1a** crystallizes in the triclinic system, in which two crystallographically independent molecules exist. The two molecules have similar conformation in which two salicylidene moieties are apart from each other (Figure 1). The torsion angles of the C−C bond and one C−O bond in the linkage N−O−CH_2−CH_2−O−N are in

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TABLE 2. Selected Torsion Angles (deg) of Salamo Ligands 1a, 1b, 1c, and 4

	1a (A[a])	**1a** (B[a])	**1b**	**1c** (A[a])	**1c** (B[a])	**4**
C−C=N−O	−179.63(13)	−179.44(14)	179.0(5)	−178.4(2)	177.4(2)	177.5(2)
C=N−O−C	178.39(13)	−179.51(14)	178.6(5)	176.9(2)	176.2(2)	−178.1(2)
N−O−C−C	−67.09(17)	−69.92(18)	177.6(6)	−68.6(3)	168.2(2)	70.5(3)
O−C−C−O	−59.97(18)	−65.12(19)	180	65.3(5)	−77.4(5)	−76.7(3)
C−C−O−N	179.50(13)	176.40(13)				−178.6(2)
C−O−N=C	−175.51(15)	178.82(15)				−174.4(2)
O−N=C−C	−179.88(14)	178.96(14)				−179.1(2)

[a] Crystallographically independent molecules.

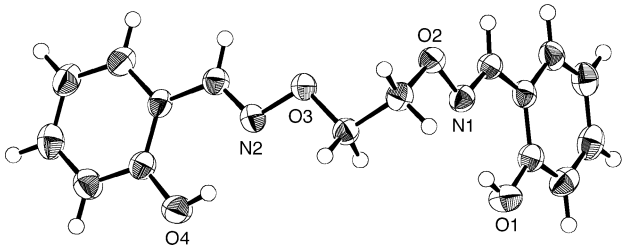


FIGURE 1. Crystal structure of **1a**. One of the crystallographically independent molecules is shown. Thermal ellipsoids are plotted at 50% probability level.

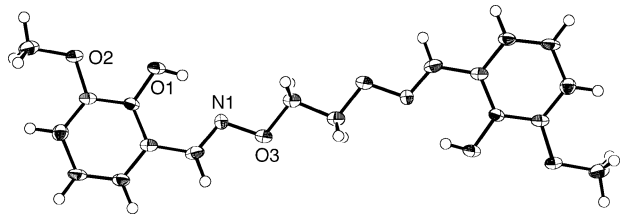


FIGURE 2. Crystal structure of **1b**. Thermal ellipsoids are plotted at 50% probability level.

the range of 60−70°, while those of the N−O bond and the other C−O bond are around 180° (Table 2). The two successive bonds in a gauche conformation make the molecule nonplanar, folded at the center of the molecule.

On the other hand, the methoxy derivative **1b** has almost planar conformation in which two salicylaldoxime moieties are apart from each other (Figure 2). There is a crystallographic center of symmetry at the middle point of the C−C bond. All the torsion angles around the C−C, C−O, and O−N bonds in the linkage are about 180°, indicating the all-trans conformation (Table 2).

Compound **1c**, which has two *tert*-butyl groups at each salicylaldoxime moiety, adopts an extended form (Figure 3). The unit cell contains two crystallographically independent molecules with different conformations, although both molecules have a crystallographically imposed twofold axis. The linkage of the molecule A contains three bonds in a gauche conformation (C−C bond and two C−O bonds), whereas molecule B has only one (C−C bond).

The structure of unsymmetrical derivative **4**, which has two different salicylaldoxime moieties, was also determined by X-ray crystallography (Figure 4). The C−C bond and one C−O bond have a gauche conformation (torsion angles: 76.7 and 70.5°, respectively), whereas the other C−O bond has an anti conformation.

In all cases, intramolecular hydrogen bonds are found between the hydroxyl groups and the oxime nitrogen while there are no intermolecular hydrogen bonds. The

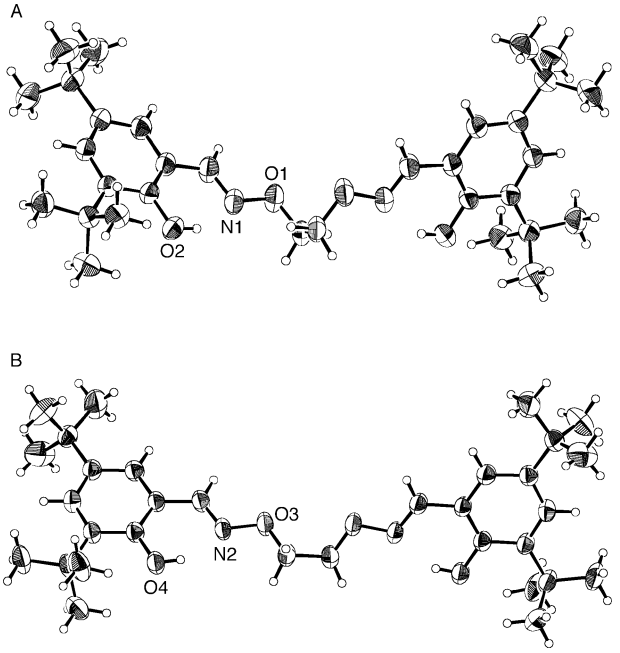


FIGURE 3. Crystal structure of **1c**. Two crystallographically independent molecules, A and B, are shown. Thermal ellipsoids are plotted at 30% probability level.

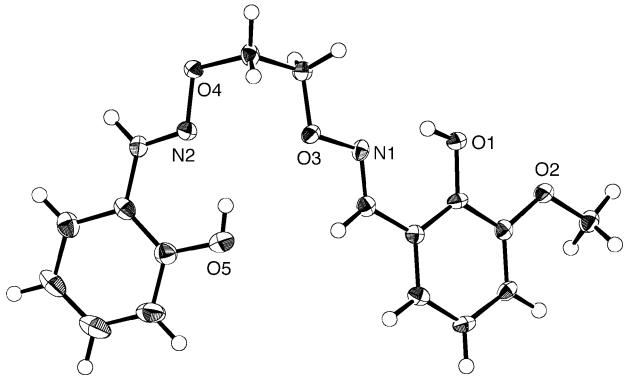


FIGURE 4. Crystal structure of unsymmetrical ligand **4**. Thermal ellipsoids are plotted at 50% probability level.

O−N distances between the hydroxyl groups and the oxime nitrogen atoms are in the range of 2.60−2.68 Å (Table 3), indicating strong O−H···N hydrogen bonds. Observation of OH resonance at 9.7−10.4 ppm in the ^{1}NMR spectra also supports the hydrogen bonding. The hydrogen bonds should stabilize the *E* geometry of the oxime bonds. Generally, salicylaldimine derivatives exist as a mixture of two tautomers, that is, imine-OH and keto-NH forms, in solution.[26] In some cases, the keto-

TABLE 3. Selected Interatomic Distances (Å) of Salamo Ligands 1a, 1b, 1c, and 4

	1a (A[a])	**1a** (B[a])	**1b**	**1c** (A[a])	**1c** (B[a])	**4**	SA1[b]	SA2[c]
O−H···N[d]	2.677(2)	2.641(2)	2.631(6)	2.650(3)	2.606(3)	2.635(3)	2.597	2.514
	2.637(2)	2.632(2)				2.642(4)		
C−OH	1.361(2)	1.352(2)	1.367(6)	1.364(3)	1.360(3)	1.360(3)	1.350(2)	1.310(1)
	1.356(2)	1.354(2)				1.362(4)		
$C_{OH}-C_{ArC=N}$	1.402(2)	1.410(3)	1.396(7)	1.396(4)	1.396(3)	1.398(4)	1.412(3)	1.433(2)
	1.405(3)	1.401(3)				1.400(4)		
$C_{Ar}-C_{C=N}$	1.454(3)	1.454(2)	1.458(8)	1.454(4)	1.454(3)	1.458(4)	1.457(3)	1.425(1)
	1.449(2)	1.453(2)				1.454(4)		
C=N	1.281(2)	1.277(2)	1.284(7)	1.273(3)	1.273(3)	1.277(4)	1.291(2)	1.308(1)
	1.274(2)	1.271(2)				1.275(4)		

[a] Crystallographically independent molecules. [b] 4-Chloro-2-(phenyliminomethyl)phenol. This compound exists exclusively as imine-OH form in the crystalline state at 90 K (ref 27). [c] 4-Chloro-2-((4-hydroxyphenyl)iminomethyl)phenol. This compound exists exclusively as keto-NH form in the crystalline state at 90 K (ref 27). [d] The distances between O and N in the O−H···N hydrogen bonds.

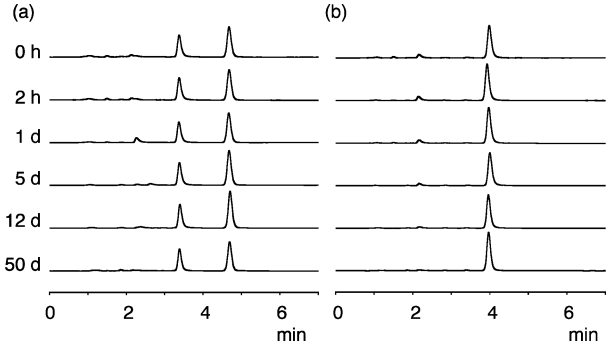


FIGURE 5. Chromatograms of HPLC for analysis of stability of salamo derivatives. (a) Equimolar mixture of **1a** and **1b** and (b) **4** in H_2O/MeCN (5:95) at 40 °C monitored by HPLC.

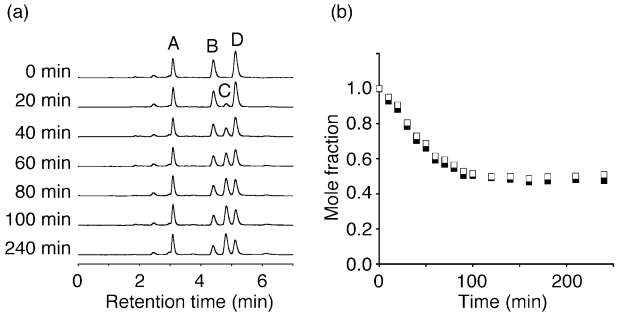


FIGURE 6. (a) Metathesis reaction of salen derivatives **9a** and **9b** in H_2O/MeCN (5:95) at 40 °C monitored by HPLC. A: benzamide (internal standard), B: **9b**, C: scrambled product (**10**), D: **9a**. (b) Time dependence of mole fraction of **9a** (filled squares) and **9b** (open squares) determined by HPLC.

NH form can be also observed in the crystalline state. However, the bond distances of the C−OH (1.35−1.37 Å) and C=N (1.27−1.28 Å) of the salamo derivatives are almost the same as those of 4-chloro-2-(phenyliminomethyl)phenol, which exists exclusively as imine-OH form (Table 3).[27] The results strongly indicate that the oxime-OH form is more favorable in the crystalline state in the salamo ligands. The observation is consistent with the absence of the band at 400 nm in the absorption spectra of **1**.

Stability of Unsymmetrical Salamo Ligands. Kinetic stability of the salamo derivatives against the C=N metathesis reaction was studied by comparison with the corresponding salen derivatives. An equimolar mixture of **1a** and **1b** was heated at 40 °C in H_2O/MeCN (5:95) solution (10 mM) and the reaction was monitored by HPLC (Figure 5, a). The retention times of **1a** and **1b** are 4.6 and 3.3 min, respectively. Even after 50 d, no reaction took place. In addition, unsymmetrical ligand **4** is also stable under similar conditions (Figure 5, b). These results indicate that the forward and reverse reactions of the equilibrium involving the C=N exchange of **1a**, **1b**, and **4** are slow. Since the conversion of the reaction is estimated to be less than 5%, the half-life time is calculated to be $>7 \times 10^5$ min.

In contrast, the corresponding salen derivatives are much less stable. Heating an equimolar mixture of **9a** and **9b** resulted in a new peak of the scrambled product **10** at 4.8 min. The intensity of the new peak increased as those of **9a** and **9b** at 5.1 and 4.4 min, respectively, became smaller (Figure 6, a). After 2 h, the scrambling reaction reached equilibrium in which the ratio of **9a**, **9b**, and **10** is nearly 1:1:2 (Figure 6, b). Under these conditions, the half-life of the reaction is around 30 min.[28] The scrambling also took place in $CDCl_3$ containing a small amount of water.[22a] From these results, salamo ligands are at least 10^4 times more stable against the metathesis reaction in H_2O/MeCN (5:95) at 40 °C than the salen ligands (Scheme 4).

Stability of Monooximes. Since the synthetic difficulty of unsymmetrical salen derivatives is mainly attributed to the instability of monoimine derivatives,[15] investigation of the stability of monooxime derivatives **3** is important.[29] The signals of 1,2-bis(aminooxy)ethane and salamo derivative **1b** were not observed in the ^1H NMR spectrum when a solution of the monooxime **3b** in $CDCl_3$ was allowed to stand for 50 d. Similarly, the reaction of salamo derivative **1b** with 1,2-bis(aminooxy)-ethane did not give monooxime **3b**. Thus, the disproportionation equilibrium of **3b** is very slow. These results indicate that the monooxime **3b** is sufficiently stable in $CDCl_3$. On the other hand, the reaction of salen **9b** with ethylenediamine in $CDCl_3$ completed in 1−2 min to give an equilibrated mixture containing **9b**, ethylenediamine,

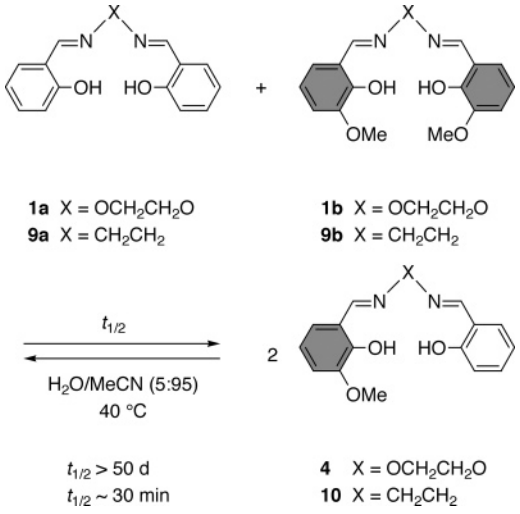
(26) Dudek, G. O.; Dudek, E. P. *J. Am. Chem. Soc.* **1966**, *88*, 2407−2412.

(27) Ogawa, K.; Kasahara, Y.; Ohtani, Y.; Harada, J. *J. Am. Chem. Soc.* **1998**, *120*, 7107−7108.

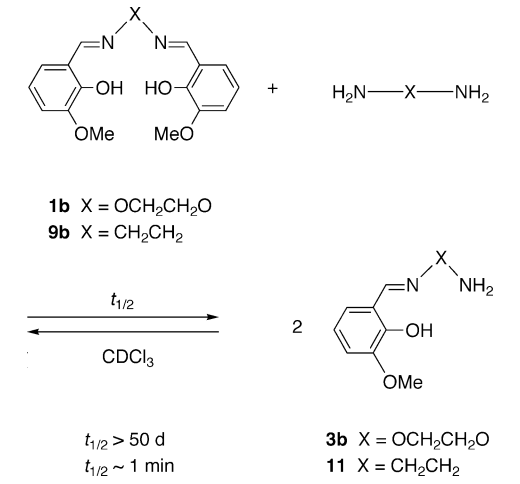
(28) The rate constants for forward and reverse reactions of the scrambling cannot be determined because the time dependence of mole fractions did not obey the ideal second-order kinetics, probably because of the existence of a small amount of intermediates.

(29) Polyakov, V. A.; Nelen, M. I.; Nazarpack-Kandlousy, N.; Ryabov, A. D.; Eliseev, A. V. *J. Phys. Org. Chem.* **1999**, *12*, 357−363.

SCHEME 4. Scrambling of Two Chelate Ligands



SCHEME 5. Disproportionation Equilibrium of Monooxime 3b or Monoimine 11



and monoimine **11**. The half-life of the formation of **9b** and ethylenediamine by the C=N exchange of **11** is also around 1 min. Consequently, the reaction of the disproportionation of monooxime **3b** is quite slower than that of monoimine **11** (Scheme 5).

These results indicate the extremely high stability of the salamo derivatives **1** and precursors **3**. The low reactivity of monooxime precursors **3** facilitates the synthesis of unsymmetrical salen ligands bearing two different salicylidene units at each end of the diimine bridge. In addition, the resultant salamo ligands that have two oxime bonds show sufficient stability to avoid the scrambling reaction. The results contrast sharply with the labile nature of salen ligands.

Conclusion

We have designed and synthesized a new series of salen-type chelate ligands that have two oxime bonds instead of imine bonds. The ligands are prepared by the reaction of 1,2-bis(aminooxy)ethane with 2 equivalents of salicylaldehyde derivatives under mild conditions. The metathesis of the C=N bonds of the salamo derivatives did not occur in H_2O/MeCN (5:95). Hence, the salamo derivatives are at least 10^4 times more stable than salen derivatives. Monooxime derivatives **3** were also synthesized as stable compounds, whereas imine analogues were difficult to be isolated. The stability of precursors **3** facilitates the synthesis of unsymmetrical salamo derivatives. Thus, the oxime ligands **1** and unsymmetrical analogues **4**−**8**, as well as its precursors **3**, may be promising units for the construction of multidentate ligands containing different kinds of C=N metal-chelate sites.

Experimental Section

General Procedure for the Synthesis of Symmetrical Salamo Ligands 1. A solution of 1,2-bis(aminooxy)ethane (0.25 mmol) in ethanol (5 mL) was added to a solution of salicylaldehyde derivative (0.50 mmol) in ethanol (5 mL) and the mixture was heated at 50−55 °C for 1−2 h. After cooling to room temperature, white precipitates were collected on a suction filter to give salamo compound **1**.

1a. Obtained from 2-hydroxybenzaldehyde (491 mg, 4.02 mmol) and 1,2-bis(aminooxy)ethane (185 mg, 2.01 mmol) in 83% yield as colorless crystals, mp 113−114 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49 (s, 4H), 6.91 (t, J = 7.6 Hz, 2H), 6.99 (d, J = 7.6 Hz, 2H), 7.17 (dd, J = 7.6, 1.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 8.25 (s, 2H), 9.75 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.0 (CH_2), 116.2 (C), 116.8 (CH), 119.7 (CH), 130.9 (CH), 131.4 (CH), 152.3 (CH=N), 157.4 (C). Anal. calcd for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N. 9.33. Found: C, 63.54; H, 5.52; N, 9.16.

1b. Obtained from 2-hydroxy-3-methoxybenzaldehyde (199.2 mg, 1.31 mmol) and 1,2-bis(aminooxy)ethane (60.3 mg, 0.655 mmol) in 79% yield as colorless crystals, mp 132−134 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 6H), 4.49 (s, 4H), 6.83 (dd, J = 7.9, 1.9 Hz, 2H), 6.86 (t, J = 7.9 Hz, 2H), 6.91 (dd, J = 7.9, 1.9 Hz, 2H), 8.26 (s, 2H), 9.74 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.2 (CH_3), 73.0 (CH_2), 113.5 (CH), 116.5 (C), 119.4 (CH), 122.4 (CH), 147.1 (C), 148.2 (C), 152.0 (CH=N). Anal. calcd for $C_{18}H_{20}N_2O_6$: C, 59.99; H, 5.59; N, 7.77. Found: C, 59.97; H, 5.87; N, 7.61.

1c. Obtained from 3,5-di(*tert*-butyl)-2-hydroxybenzaldehyde (522.0 mg, 2.23 mmol) and 1,2-bis(aminooxy)ethane (102.6 mg, 1.11 mmol) in 74% yield. The sample was purified by recrystallization from chloroform/hexane to give colorless crystals, mp 113−115 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 18H), 1.43 (s 18H), 4.48 (s, 4H), 6.98 (d, J = 2.5 Hz, 2H), 7.34 (d, J = 2.5 Hz, 2H), 8.26 (s, 2H), 10.15 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.5 (CH_3), 31.5 (CH_3), 34.1 (C), 35.1 (C), 73.0 (CH_2), 115.6 (C), 125.7 (CH), 126.2 (CH), 136.4 (C), 141.2 (C), 153.4 (CH=N), 154.3 (C). Anal. calcd for $C_{32}H_{48}N_2O_4\cdot0.25H_2O$: C, 72.62; H, 9.24; N, 5.29. Found: C, 72.41; H, 8.98; N, 5.23.

1d. Obtained from 2-hydroxy-3-methylthiobenzaldehyde[30] (84.2 mg, 0.50 mmol) and 1,2-bis(aminooxy)ethane (23.1 mg, 0.25 mmol) in 74% as colorless crystals, mp 107−108 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 6H), 4.47 (s, 4H), 6.91 (t, J = 7.7 Hz, 2H), 7.03 (dd, J = 7.7, 1.4 Hz, 2H), 7.21 (dd, J = 7.7, 1.4 Hz, 2H), 8.24 (s, 2H), 10.35 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1 (CH_3), 73.0 (CH_2), 115.5 (C), 120.0 (CH), 125.8 (C), 127.9 (CH), 128.9 (CH), 151.9 (CH=N), 154.4 (C). Anal. calcd for $C_{18}H_{20}N_2O_4S_2$: C, 55.08; H, 5.14; N, 7.14. Found: C, 54.92; H, 5.06; N, 7.01.

1e. Obtained from 5-bromo-2-hydroxybenzaldehyde (100.5 mg, 0.50 mmol) and 1,2-bis(aminooxy)ethane (23.0 mg, 0.25 mmol) in 64% as colorless crystals, mp 144.5−145.5 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48 (s, 4H), 6.87 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 2.5 Hz, 2H), 7.36 (dd, J = 8.6, 2.5 Hz, 2H), 8.14 (s, 2H), 9.74 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.3 (CH_2), 111.2 (C), 117.8 (C), 118.7 (CH), 132.9 (CH), 134.0 (CH),

(30) Ando, M.; Emoto, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2435−2436.

151.0 (CH=N), 156.4 (C). Anal. calcd for $C_{16}H_{14}Br_2N_2O_4$: C, 41.95; H, 3.08; N, 6.12. Found: C, 41.78; H, 3.04; N, 6.06.

1f. Obtained from 2,5-dihydroxybenzaldehyde (93.0 mg, 0.67 mmol) and 1,2-bis(aminooxy)ethane (30.6 mg, 0.33 mmol) in 77% as colorless crystals, mp 236.5−237.5 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.33 (s, 4H), 6.67 (dd, J = 8.8, 2.4 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 2.4 Hz, 2H), 8.31 (s, 2H), 9.02 (s, 2H), 9.34 (s, 2H), ^{13}C NMR (100 MHz, DMSO-d_6) δ 72.5 (CH_2), 112.6 (CH), 117.5 (CH), 118.1 (C), 119.3 (CH), 147.3 (CH=N), 149.4 (C), 150.3 (C). Anal. calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.57; H, 4.86; N, 8.17.

1g. Obtained from 2,3-dihydroxybenzaldehyde[31] (276.4 mg, 2.0 mmol) and 1,2-bis(aminooxy)ethane (92.0 mg, 1.0 mmol) in 88% as colorless crystals, mp 111.5−112.5 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (s, 4H), 5.56 (s, 2H), 6.74 (dd, J = 7.8, 1.6 Hz, 2H), 6.83 (t, J = 7.8 Hz, 2H), 6.97 (dd, J = 7.8, 1.6 Hz, 2H), 8.22 (s, 2H), 9.89 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.1 (CH_2), 115.9 (C), 116.7 (CH), 120.2 (CH), 121.9 (CH), 144.1 (C), 144.7 (C), 152.1 (CH=N). Anal. calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.75; H, 4.86; N, 8.25.

1h. Obtained from 2-hydroxy-5-nitrobenzaldehyde[32] (83.7 mg, 0.50 mmol) and 1,2-bis(aminooxy)ethane (23.0 mg, 0.25 mmol) in 79% as colorless crystals, mp 202−203 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.43 (s, 4H), 7.01 (d, J = 9.2 Hz, 2H), 8.10 (dd, J = 9.2, 2.6 Hz, 2H), 8.359 (d, J = 2.6 Hz, 2H), 8.362 (s, 2H), the OH signal was not observed, ^{13}C NMR (100 MHz, DMSO-d_6) δ 73.1 (CH_2), 117.1 (CH), 118.9 (C), 122.7 (CH), 127.1 (CH), 140.2 (C), 144.7 (CH=N), 162.0 (C). Anal. calcd for $C_{16}H_{14}N_4O_8$: C, 49.24; H, 3.62; N, 14.35. Found: C, 49.12; H, 3.69; N, 14.00.

General Procedure for the Synthesis of Monooxime Ligands 3. A solution of 1,2-bis(aminooxy)ethane (92 mg, 1.0 mmol) in ethanol (2 mL) was added to a solution of salicylaldehyde derivative (0.50 mmol) in ethanol (2 mL) and the mixture was heated at 50−55 °C for 1 h. The solution was concentrated in vacuo and the residue was purified by column chromatography (SiO_2, chloroform/ethyl acetate, 50:1) to afford oil or crystals of **3**.

3a. Prepared from 2-hydroxybenzaldehyde (245 mg, 2.01 mmol) and 1,2-bis(aminooxy)ethane (368 mg, 4.00 mmol) in 81% as colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (t, J = 4.6 Hz, 2H), 4.37 (t, J = 4.6 Hz, 2H), 5.53 (brs, 2H), 6.91 (t, J = 7.7 Hz, 1H), 6.98 (d, J = 7.7 Hz, 1H), 7.16 (dd, J = 7.7, 1.4 Hz, 1H), 7.28 (t, J = 7.7 Hz, 1H), 8.22 (s, 1H), 9.82 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.6 (CH_2), 73.7 (CH_2), 116.2 (C), 116.7 (CH), 119.6 (CH), 130.7 (CH), 131.2 (CH), 151.3 (CH=N), 157.3 (C). Anal. calcd for $C_9H_{12}N_2O_3\cdot0.2H_2O$: C, 54.10; H, 6.26; N, 14.02. Found: C, 54.38; H, 6.10; N, 13.68.

3b. Prepared from 2-hydroxy-3-methoxybenzaldehyde (644 mg, 4.23 mmol) and 1,2-bis(aminooxy)ethane (774 mg, 8.40 mmol) in 71% yield as colorless crystals after recrystallization (chloroform/hexane), mp 96−97 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 3H), 3.97 (t, J = 4.4 Hz, 2H), 4.37 (t, J = 4.4 Hz, 2H), 5.52 (brs, 2H), 6.81 (dd, J = 7.7, 1.6 Hz, 1H), 6.86 (t, J = 7.7 Hz, 1H), 6.91 (dd, J = 7.7, 1.6 Hz, 1H), 8.23 (s, 1H), 9.87 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.0 (CH_3), 72.5 (CH_2), 73.6 (CH_2), 113.2 (CH), 116.4 (C), 119.3 (CH), 122.1 (CH), 146.9 (C), 148.0 (C), 151.3 (CH=N). Anal. calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.24; N, 12.38. Found: C, 52.90; H, 6.26; N, 12.27.

3c. Prepared from 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (117.2 mg, 0.50 mmol) and 1,2-bis(aminooxy)ethane (92.1 mg, 1.0 mmol) in 82% as pale yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 9H), 1.44 (s, 9H), 3.98 (t, J = 4.8 Hz, 2H), 4.36 (t, J = 4.8 Hz, 2H), 5.52 (brs, 2H), 6.97 (d, J = 2.0 Hz, 1H), 7.35 (d, J = 2.0 Hz, 1H), 8.22 (s, 1H), 10.12 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.4 (CH_3), 31.5 (CH_3), 34.1 (C), 35.1 (C), 72.5 (CH_2), 73.7 (CH_2), 115.6 (C), 125.6 (CH), 126.2 (CH), 136.4 (C), 141.2 (C), 153.2 (CH=N), 154.3 (C). Anal. calcd for $C_{17}H_{28}N_2O_3\cdot0.25H_2O$: C, 65.25; H, 9.18; N, 8.95. Found: C, 65.33; H, 8.91; N, 8.75.

3d. Prepared from 2-hydroxy-3-methylthiobenzaldehyde (84.1 mg, 0.50 mmol) and 1,2-bis(aminooxy)ethane (92.1 mg, 1.0 mmol) in 86% yield as pale yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3H), 3.97 (t, J = 4.5 Hz, 2H), 4.37 (t, J = 4.5 Hz, 2H), 5.52 (brs, 2H), 6.92 (t, J = 7.6 Hz, 1H), 7.02 (dd, J = 7.6, 1.4 Hz, 1H), 7.22 (dd, J = 7.6, 1.4 Hz, 1H), 8.21 (s, 1H), 10.42 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1 (CH_3), 72.8 (CH_2), 73.6 (CH_2), 115.6 (C), 120.0 (CH), 125.9 (C), 127.8 (CH), 128.8 (CH), 151.5 (CH=N), 154.4 (C). Anal. calcd for $C_{10}H_{14}N_2O_3S\cdot0.2H_2O$: C, 48.84; H, 5.90; N, 11.39. Found: C, 48.98; H, 5.80; N, 10.99.

3e. Prepared from 5-bromo-2-hydroxybenzaldehyde (100.5 mg, 0.50 mmol) and 1,2-bis(aminooxy)ethane (92.1 mg, 1.0 mmol) in 59% as colorless crystals, mp 60−61 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (t, J = 4.5 Hz, 2H), 4.38 (t, J = 4.5 Hz, 2H), 5.53 (brs, 2H), 6.88 (d, J = 9.0 Hz, 1H), 7.27 (d, J = 2.5 Hz, 1H), 7.36 (dd, J = 9.0, 2.5 Hz, 1H), 8.13 (s, 1H), 9.85 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.9 (CH_2), 73.7 (CH_2), 111.2 (C), 118.0 (C), 118.6 (CH), 132.7 (CH), 133.8 (CH), 150.5 (CH=N), 156.4 (C). Anal. calcd for $C_9H_{11}BrN_2O_3$: C, 39.29; H, 4.03; N, 10.18. Found: C, 39.73; H, 3.97; N, 10.02.

General Procedure for the Synthesis of Unsymmetrical Salamo Ligands 4−8. A solution of monooxime **3** (0.10 mmol) in ethanol (2 mL) was added to a solution of salicylaldehyde derivative (0.10 mmol) in ethanol (2 mL) and the mixture was heated at 50−55 °C for 1 h. After cooling to room temperature, white precipitates were collected on a suction filter to give colorless crystals of **4**−**8**.

4. Prepared from monooxime **3b** (90.5 mg, 0.40 mmol) and 2-hydroxybenzaldehyde (48.8 mg, 0.40 mmol) in 56% as colorless crystals after recrystallization (chloroform/hexane), mp 80−81 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 3H), 4.49 (s, 4H), 6.82 (dd, J = 7.6, 1.7 Hz, 1H), 6.86 (t, J = 7.6 Hz, 1H), 6.90 (t, J = 7.8 Hz, 1H), 6.92 (dd, J = 7.6, 1.7 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 7.16 (dd, J = 7.8, 1.7 Hz, 1H), 7.28 (t, J = 7.8 Hz, 1H), 8.24 (s, 1H), 8.25 (s, 1H), 9.74 (s, 1H), 9.75 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.1 (CH_3), 72.9 (CH_2), 73.1 (CH_2), 113.5 (CH), 116.1 (C), 116.4 (C), 116.7 (CH), 119.4 (CH), 119.6 (CH), 122.4 (CH), 130.9 (CH), 131.3 (CH), 147.1 (C), 148.1 (C), 151.9 (CH=N), 152.3 (CH=N), 157.4 (C). Anal. calcd for $C_{17}H_{18}N_2O_5$: C, 61.81; H, 5.49; N, 8.48. Found: C, 61.69; H, 5.56; N, 8.34.

5. Prepared from monooxime **3b** (22.6 mg, 0.10 mmol) and 2-hydroxy-3-methylthiobenzaldehyde (16.8 mg, 0.10 mmol) in 66% as colorless crystals, mp 117−117.5 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 3.90 (s, 3H), 4.48 (s, 4H), 6.82 (dd, J = 7.9, 2.3 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.91 (dd, J = 7.8, 2.3 Hz, 1H), 7.02 (dd, J = 7.6, 1.3 Hz, 1H), 7.21 (dd, J = 7.6, 1.3 Hz, 1H), 8.23 (s, 1H), 8.26 (s, 1H), 9.71 (s, 1H), 10.36 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1 (CH_3), 56.1 (CH_3), 73.0 (CH_2), 73.1 (CH_2), 113.5 (CH), 115.5 (C), 116.4 (C), 119.4 (CH), 119.9 (CH), 122.4 (CH), 125.8 (C), 127.9 (CH), 128.9 (CH), 147.0 (C), 148.1 (C), 151.8 (CH=N), 152.0 (CH=N), 154.4 (C). Anal. calcd for $C_{18}H_{20}N_2O_5S\cdot0.5H_2O$: C, 56.09; H, 5.49; N, 7.27. Found: C, 55.89; H, 5.24; N, 7.14.

6. Prepared from monooxime **3b** (22.7 mg, 0.10 mmol) and 2-hydroxy-5-nitrobenzaldehyde (16.8 mg, 0.10 mmol) in 64% as colorless crystals, mp 135−136 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 4.49−4.54 (m, 4H), 6.81 (dd, J = 7.9, 1.8 Hz, 1H), 6.85 (t, J = 7.9 Hz, 1H), 6.91 (dd, J = 7.9, 1.8 Hz, 1H), 7.04 (d, J = 8.8 Hz, 1H), 8.12 (d, J = 2.7 Hz, 1H), 8.16 (dd, J = 8.8, 2.7 Hz, 1H), 8.24 (s, 1H), 8.28 (s, 1H), 9.66 (s, 1H), 10.62 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.1 (CH_3), 73.1 (CH_2), 73.7 (CH_2), 113.4 (CH), 116.2 (C), 116.3 (C), 117.5 (CH), 119.5 (CH), 122.3 (CH), 126.7 (CH), 126.8 (CH), 140.6 (C), 146.9 (C), 148.1 (C), 150.6 (CH=N), 152.0 (CH=N), 162.5 (C). Anal. calcd for $C_{17}H_{17}N_3O_7\cdot0.25H_2O$: C, 53.76; H, 4.64; N, 11.06. Found: C, 53.78; H, 4.51; N, 10.97.

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TABLE 4. Crystallographic Data for Salamo Ligands 1a, 1b, 1c, and 4[a]

	1a	1b	1c·0.25H_2O	4
formula	$C_{16}H_{16}N_2O_4$	$C_{18}H_{20}N_2O_6$	$C_{32}H_{48.5}N_2O_{4.25}$	$C_{17}H_{18}N_2O_5$
temperature (K)	180	120	296	120
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P-1$	$P2_1/n$	$C2/c$	$P2_1/n$
a (Å)	4.6416(4)	4.694(4)	33.113(5)	15.272(12)
b (Å)	15.0604(11)	14.616(6)	16.850(3)	4.628(3)
c (Å)	20.9786(14)	12.356(4)	12.654(2)	23.257(18)
α (deg)	92.323(3)			
β (deg)	93.095(3)	98.065(3)	110.583(3)	104.485(11)
γ (deg)	98.4404(16)			
V (Å^3)	1446.75(19)	839.3(9)	6609.3(18)	1591(2)
Z	4	2	8	4
D_{calc} (g/cm^3)	1.379	1.426	1.064	1.379
reflections collected	11783	5122	21236	11699
unique reflections	5613	1482	6434	3564
R_{int}	0.0411	0.2079	0.0763	0.0527
F_{000}	632	380	2308	696
$\mu_{MoK\alpha}$ (mm^{-1})	0.100	0.108	0.070	0.103
limiting indices	$-5 \le h \le 5$	$-5 \le h \le 3$	$-40 \le h \le 40$	$-18 \le h \le 19$
	$-18 \le k \le 18$	$-17 \le k \le 16$	$-20 \le k \le 20$	$-6 \le k \le 6$
	$-25 \le l \le 25$	$-14 \le l \le 14$	$-13 \le l \le 15$	$-27 \le l \le 30$
restraints/parameters	0/401	0/119	0/384	0/220
goodness of fit (F^2)	1.054	0.979	1.009	1.054
R indices ($I > 2\sigma(I)$)	$R1 = 0.0453$	$R1 = 0.0816$	$R1 = 0.0716$	$R1 = 0.0749$
	$wR2 = 0.1099$	$wR2 = 0.1696$	$wR2 = 0.1515$	$wR2 = 0.1687$
R indices (all data)	$R1 = 0.0700$	$R1 = 0.2089$	$R1 = 0.1138$	$R1 = 0.1135$
	$wR2 = 0.1213$	$wR2 = 0.2330$	$wR2 = 0.1747$	$wR2 = 0.1900$

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

7. Prepared from monooxime **3c** (30.9 mg, 0.10 mmol) and 2-hydroxybenzaldehyde (12.2 mg, 0.10 mmol) in 70%. The sample was purified by column chromatography on silica gel (chloroform) to give colorless crystals, mp 105−106 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 9H), 1.43 (s, 9H), 4.48 (s, 4H), 6.90 (td, J = 7.6, 1.0 Hz, 1H), 6.978 (d, J = 8.2 Hz, 1H), 6.980 (d, J = 2.3 Hz, 1H), 7.15 (dd, J = 7.6, 1.5 Hz, 1H), 7.28 (td, J = 7.8, 1.5 Hz, 1H), 7.35 (d, J = 2.3 Hz, 1H), 8.24 (s, 1H), 8.25 (s, 1H), 9.77 (s, 1H), 10.11 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.5 (CH_3), 31.5 (CH_3), 34.1 (C), 35.1 (C), 72.7 (CH_2), 73.2 (CH_2), 115.6 (C), 116.2 (C), 116.8 (CH), 119.6 (CH), 125.7 (CH), 126.3 (CH), 130.9 (CH), 131.3 (CH), 136.4 (C), 141.3 (C), 152.3 (CH=N), 153.4 (CH=N), 154.3 (C), 157.4 (C). Anal. calcd for $C_{24}H_{32}N_2O_4 \cdot H_2O$: C, 66.95; H, 7.96; N, 6.51. Found: C, 67.41; H, 7.80; N, 6.64.

8. Prepared from monooxime **3e** (27.5 mg, 0.10 mmol) and 2-hydroxybenzaldehyde (12.2 mg, 0.10 mmol) in 51%. The sample was purified by column chromatography on silica gel (chloroform) to give colorless crystals, mp 88−89 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47−4.50 (m, 4H), 6.87 (d, J = 8.6 Hz, 1H), 6.91 (t, J = 7.8 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 7.16 (dd, J = 7.8, 1.5 Hz, 1H), 7.27 (d, J = 2.5 Hz, 1H), 7.29 (td, J = 7.8, 1.5 Hz, 1H), 7.35 (dd, J = 8.6, 2.5 Hz, 1H), 8.15 (s, 1H), 8.23 (s, 1H), 9.72 (s, 1H), 9.77 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.0 (CH_2), 73.3 (CH_2), 111.2 (C), 116.1 (C), 116.8 (CH), 117.9 (C), 118.7 (CH), 119.7 (CH), 130.9 (CH), 131.5 (CH), 132.9 (CH), 134.0 (CH), 151.0 (CH=N), 152.4 (CH=N), 156.5 (C), 157.4 (C). Anal. calcd for $C_{16}H_{15}BrN_2O_4$: C, 50.68; H, 3.99; N, 7.39. Found: C, 50.65; H, 4.08; N, 7.22.

Metathesis Reaction of 1a and 1b. A mixture of **1a** (10 μmol) and **1b** (10 μmol) was dissolved in H_2O/MeCN (5:95, 1 mL) at 40 °C and the mixture was kept at 40.0 ± 0.1 °C. Aliquots of 5 μL were taken from the reaction mixture, diluted to the volume of 1 mL with acetonitrile, and 1 μL of the resulting solution was injected to HPLC (Shimadzu LC-10A/CLASS-VP system equipped with a Mightysil RP-8 GP150-4.6 column, eluent, H_2O/MeCN, 20:80). The reaction of **4** (10 μmol) in H_2O/MeCN (5:95, 0.5 mL) at 40 °C was monitored by HPLC in a similar manner.

Metathesis Reaction of 9a and 9b. A mixture of **9a** (20 μmol) and **9b** (20 μmol) was dissolved in H_2O/MeCN (5:95, 2 mL) and the mixture was kept at 40.0 ± 0.1 °C. Aliquots of 2 μL were taken from the reaction mixture, diluted to the volume of 1 mL with acetonitrile containing benzamide (0.2 mM, internal standard), and 1 μL of the resulting solution was injected to HPLC (Shimadzu LC-10A/CLASS-VP system equipped with a Mightysil RP-18 GP250-4.6 column, eluent, H_2O/MeCN, 50:50).

X-ray Crystallographic Analysis of 1a, 1b, 1c, and 4. Intensity data were collected on a Rigaku R-AXIS Rapid or a Rigaku Mercury CCD diffractometer with Mo$K\alpha$ radiation (λ = 0.71069 Å). Reflection data were corrected for Lorentz and polarization factors and for absorption using the multiscan method. Crystal data are collected in Table 4. The structure was solved by direct methods (SIR-97[33] or SHELXS 97[34]) and refined by full-matrix least squares on F^2 using SHELXL 97.[35] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were idealized by using the riding models.

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Supporting Information Available: Crystallographic data for **1a**, **1b**, **1c**, and **4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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