Ligand Transfer Reactions between Schiff Base Divalent Group 14 Element Species and Titanium, Nickel, Boron, and Phosphorus Halides

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Reactions of the inorganic complexes $TiCl_4$, $NiCl_2$, BF_3, PCl_3, and (Y)PCl_3 (Y = O, S), Cp_2TiCl_2, and *t*-$BuPCl_2$ with the Schiff base divalent group 14 element species $(L^2)M$ (**1**−**3**: L^2 = *N*,*N*′-bis(salicylidene)ethylenediamine (Salen), M = Ge (**1**), Sn (**2**); L^2 = (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, M = Pb (**3**)) have been investigated. $TiCl_4$ and Cp_2TiCl_2 afforded the ionic $[ClTi(L^2)]^+[MCl_3]^-$ (**4**) and the neutral $Cp(Cl)Ti(L^2)$ (**5**) complexes, respectively. With $NiCl_2$·DPPE (DPPE = 1,2-bis(diphenylphosphino)ethane) and (Salen)Sn as starting materials, substitution of tin led to the complex (Salen)Ni·$SnCl_2$ (**7**). The linear diboron compound $F_2B(Salen)BF_2$ (**9**) together with the complex (Salen)Sn·SnF_2 (**10**) were produced on reaction of BF_3·Me_2O with (Salen)Sn. With *t*-$BuPCl_2$ and PCl_3, the phosphite *t*-$BuP(L^2)$ (**11**) and the phosphocation $[(L^2)P]^+$ (**12**) together with the anion $[MCl_3]^-$ (**9**) were obtained, respectively. The phosphoryl and thiophosphoryl chlorides (Y)PCl_3 (Y = O, S) yielded the dinuclear dimeric phosphoranes (Y)P(Cl(Salen)P(Y)(C)(Salen)) (Y = O (**13**), S (**14**)). The crystal structure of **3** was determined by X-ray structure analysis.

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Introduction

Multidentate Schiff bases have been used extensively in the preparation of various complexes of transition metals and main-group elements, since such polydentate ligands provide unusual stabilization of different oxidation states as well as a rigid coordination sphere for the central element. The chemistry of these ligands is especially developed for transition metals[1] because of their catalytic properties. However, few papers have described Schiff base complexes of elements of groups 4,[2] 13,[3] and 14,[3o,4] and no group 15 complex incorporating a Salen type ligand has yet been reported.

All such complexes are frequently prepared by the relatively straightforward reaction of the appropriate halide with a Schiff base alcohol, but often side reactions resulting from the presence of HX byproducts are observed. Therefore, after our studies on the stable subvalent group 14 element species $(L^2)M$[5,6] and $(L^2)M{=}E$[6] and their related transition-metal complexes $[(L^2)M]_nM'L'_m$ [7,8] (L^2 = tetradentate Schiff base; M = Ge, Sn, Pb; E = S, Se, NR; *n* = 1, $M'L'_m$ = $W(CO)_5$, $Cr(CO)_5$, $Fe(CO)_4$, $Mn(Cp)(CO)_2$; *n* = 2, $M'L'_m$ = $W(CO)_4$, $Cr(CO)_4$),[7,8] we sought to explore the potential of the $(L^2)M$ species in exchange reactions for syntheses of transition-metal and main-group-element Schiff base complexes under mild conditions. Herein, we report the reactions of the inorganic halides $TiCl_4$, $NiCl_2$, BF_3, PCl_3, and (Y)PCl_3 (Y = O, S) and of Cp_2TiCl_2 and *t*-$BuPCl_2$ with the divalent group 14 element species $(L^2)M$ (L^2 = *N*,*N*′-bis(salicylidene)ethylenediamine (Salen), M = Ge (**1**), Sn (**2**); L^2 = (*R*,*R*)-(−)-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, M = Pb (**3**)). The syntheses and physicochemical characterization of

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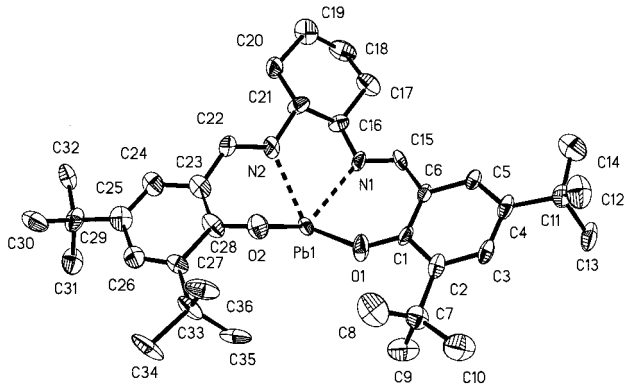

Figure 1. Molecular structure of **3**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3

Distances			
Pb(1)−O(1)	2.203(12)	O(1)−C(1)	1.33(2)
Pb(1)−O(2)	2.345(12)	O(2)−C(28)	1.33(2)
Pb(1)−N(1)	2.454(14)	N(1)−C(16)	1.41(2)
Pb(1)−N(2)	2.486(15)	N(2)−C(21)	1.48(2)
Angles			
O(1)−Pb(1)−O(2)	82.6(5)	C(15)−N(1)−C(16)	123.8(15)
O(1)−Pb(1)−N(1)	78.2(5)	C(15)−N(1)−Pb(1)	122.8(11)
O(2)−Pb(1)−N(1)	115.1(5)	C(16)−N(1)−Pb(1)	112.5(11)
O(1)−Pb(1)−N(2)	116.1(5)	C(22)−N(2)−C(21)	121.8(15)
O(2)−Pb(1)−N(2)	70.0(5)	C(22)−N(2)−Pb(1)	115.6(12)
N(1)−Pb(1)−N(2)	65.0(4)	C(21)−N(2)−Pb(1)	120.2(10)
C(1)−O(1)−Pb(1)	138.9(11)	N(2)−C(21)−C(16)	106.1(14)
C(28)−O(2)−Pb(1)	109.0(10)	N(1)−C(16)−C(21)	109.5(13) 16

the starting materials **1**−**3**,[5,6] including single crystal X-ray data for **2**, have been recently reported; complementarily, an X-ray crystal structure determination of the chiral plumbylene **3** has been carried out in this work.

Results and Dicussion

Crystalline Structure of 3. Diffraction-quality single crystals were obtained by slow crystallization from toluene. Figure 1 shows the solid-state structure of **3**. As in various previously reported (L^2)M divalent species,[4k,6,9] in particular in the plumbylene [Salen$^{t-Bu,Me}$]Pb,[9] the metal center is at the apex of a distorted square pyramid, the Pb atom being displaced by 1.23 Å from the nearly perfect plane N_2O_2 (maximum deviation 0.004 Å). The tetradentate bonding of the ligand affords Pb−O bond distances of 2.203(12) and 2.345(12) Å and Pb−N bond distances of 2.454(14) and 2.486(15) Å (Figure 1). Selected bond lengths and angles are given in Table 1. The Pb−O bonds are slightly longer than typical σ Pb−O bonds (2.15 Å);[10] the Pb−N distances are within the normal range for these species (typical σ Pb−N 2.24 Å).[11] In the crystal, due primarily to Pb−O and accessorily Pb−N intermolecular interactions, the plumbylene molecules are stacked on a 4-fold screw axis (Figure 2). The stacked systems are not perpendicular with respect to the stacking axis but are tilted by an angle of roughly 10°. The shortest intermolecular distances between Pb of one molecule (d(A)) and the distorted square N_2O_2 of the quadridentate ligand of one vicinal molecule (B) are $Pb_A-O_{1B} = 3.184$ Å and $Pb_A-N_{1B} = 3.791$ Å, the other Pb_A−square N_2O_2 distances being 3.994 Å (Pb_A-O_{2B}) and 4.467 Å (Pb_A-N_{2B}). It is noteworthy that the Pb_A-O_{1B} and Pb_A-N_{1B} bonds are significantly shorter than the sum of van der Waals radii (Pb−O = 4.02 Å and Pb−N = 4.05 Å).[12] It is worth underlining the fact that in benzene-d_6 solution the ^{207}Pb NMR spectrum of **3** (δ 141.5 ppm) is also consistent with a monomeric N_2O_2 tetracoordinate bivalent species.

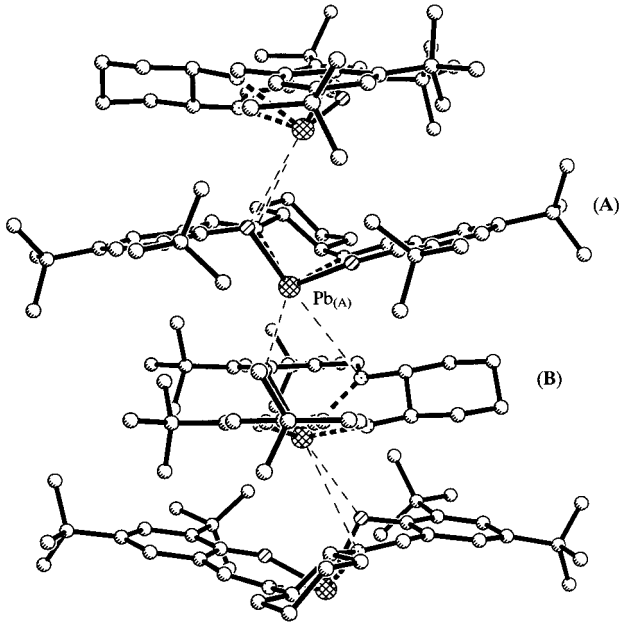

Figure 2. Stacking of **3** in solid state.

Interactions of the (L^2)M Species 1−3 with the Titanium Halides $TiCl_4$ and Cp_2TiCl_2. Treatment of the (L^2)M divalent species **1**−**3**[5] with a solution of $TiCl_4$ in methylene chloride at room temperature afforded the ionic metal(II) complexes $[ClTi(L^2)]^+[MCl_3]^-$ (**4**) in nearly quantitative yield (Scheme 1). Compound **4** gave satisfactory microanalytical as well as ^{1}H NMR, IR, FAB mass (glycerol), and ^{119}Sn NMR (in case of the tin compound) data. Although no complex of formula $[R_2TiCl]^+[MCl_3]^-$ has previously been reported, the existence of the $[MCl_3]^-$ anions is well recognized and, in particular, $SnCl_3^-$ has been detected by ^{119}Sn NMR in a variety of ionic complexes.[13]

To obtain the complex Cp_2Ti(Salen), we treated Cp_2TiCl_2 with 1 equiv of (Salen)Sn. This reaction, effected at room temperature, gave a reddish brown solid. The proton NMR spectrum of the latter displayed two resonances for the Cp ligand (6.37 and 6.02 ppm) which indicated the presence of two compounds (major m and minor n) whose m/n ratio is 60/40 (revealed by integration) and a multiplet for the CH_2 corresponding to the Salen group. Attempts at purification by crystallization from a variety of solvents (toluene, THF, pentane) permitted removal of a major part of the known divalent

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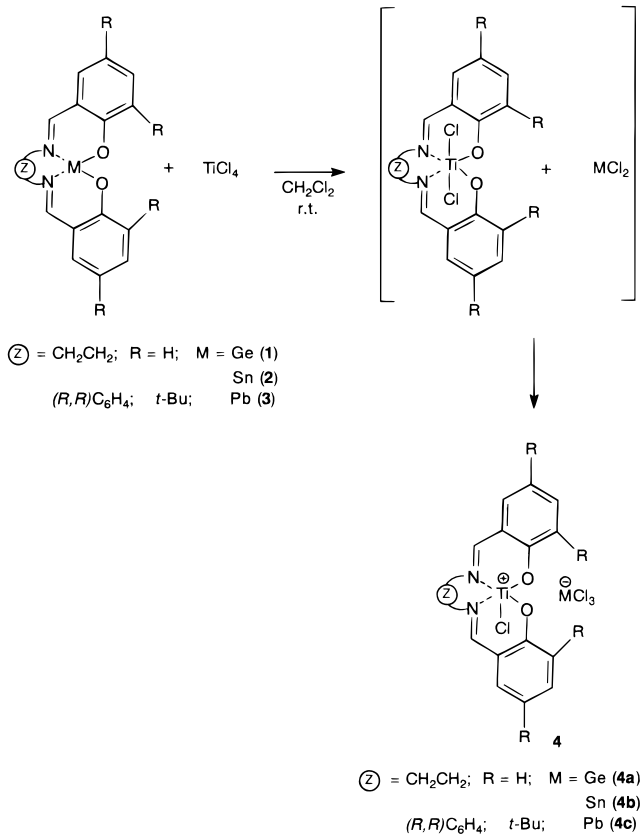
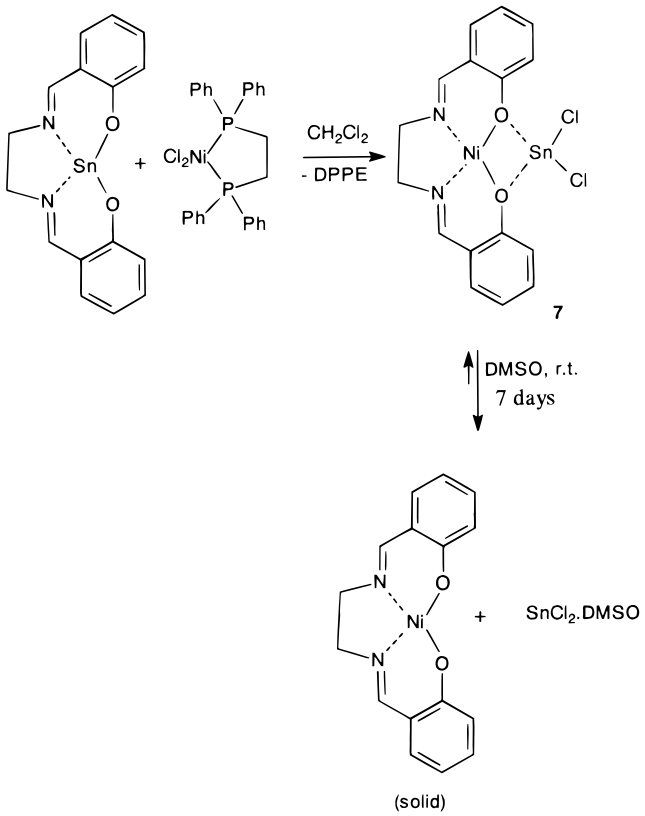
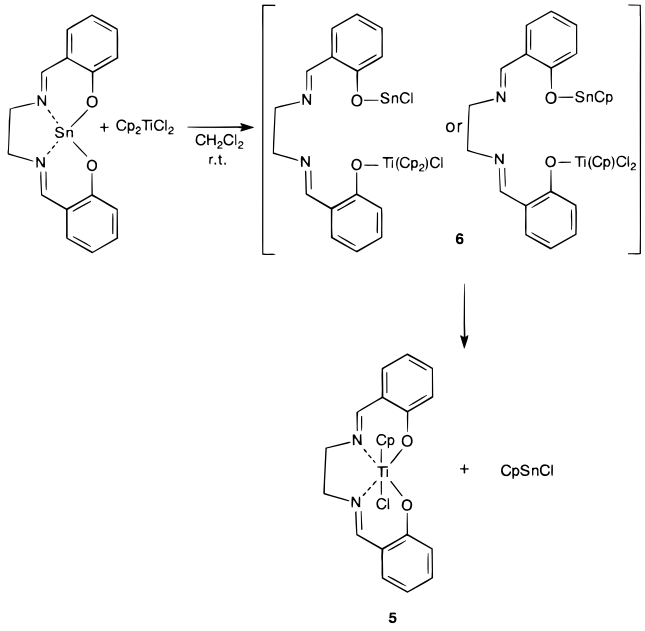
Scheme 1



Scheme 2



Scheme 3



species $CpSnCl$[14] from this mixture and isolation of Cp(Cl)Ti(Salen) (**5**), but X-ray-quality crystals could not be obtained. This reaction most likely proceeds via the heteroleptic intermediate stannylene **6** (characterized by FAB but, unfortunately, not by ^{119}Sn NMR, which would have allowed its precise identification and thus determine whether the first exchange involved the Cp ligand or the Cl atom) (Scheme 2).

Interaction of (Salen)Sn with the Nickel Halide Complex $NiCl_2$·DPPE (DPPE = 1,2-Bis(diphenylphosphino)ethane). Similarly, substitution of tin for nickel in (Salen)Sn was observed upon mixing a concentrated methylene chloride solution of the $NiCl_2$·DPPE complex and the stannylene (Salen)Sn. The product was (Salen)Ni·$SnCl_2$ (**7**) (Scheme 3). This is believed to be a consequence of an exchange reaction of (Salen)Sn with $NiCl_2$ to give (Salen)Ni,[17] followed by the reaction of the latter with $SnCl_2$ due to the availability of the Schiff base oxygen sites of (Salen)Ni, which acts as a bidentate oxygen donor ligand.[15,16] Complex **7** was characterized by FAB, by elemental analysis, and by a signal at −334 ppm in the ^{119}Sn NMR spectrum. It was impossible to obtain crystals suitable for X-ray determination, since relatively dilute DMSO solutions of (Salen)Ni·$SnCl_2$ yielded red-brown crystals of the known (Salen)Ni after several days. It is noteworthy that we have also observed formation of a 1/1 adduct (**8**) by mixing $SnCl_2$ and (Salen)Sn in methylene chloride. Its ^{119}Sn NMR showed two resonances at −336 and -554 ppm (pure $SnCl_2$ and (Salen)Sn appearing in DMSO-d_6 respectively at −380 and −580 ppm); these chemical shifts are consistent with the phenolic oxygens of the Salen ligand of the Sn(Salen) moiety being complexed to the tin atom of $SnCl_2$ (Scheme 4).

Interaction of (Salen)Sn with the Boron Halide Complex BF_3·Me_2O. Treatment of BF_3·Me_2O with 1 equiv of (Salen)Sn resulted in formation of the complex F_2Sn·Sn(Salen) (**10**), together with the diboron com-

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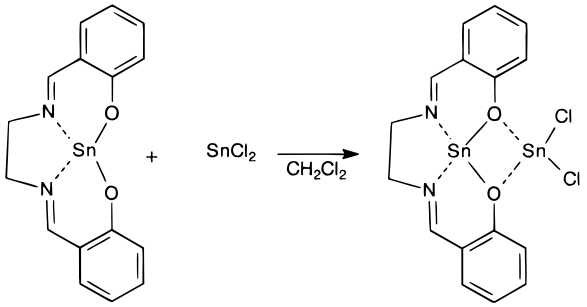
Scheme 4



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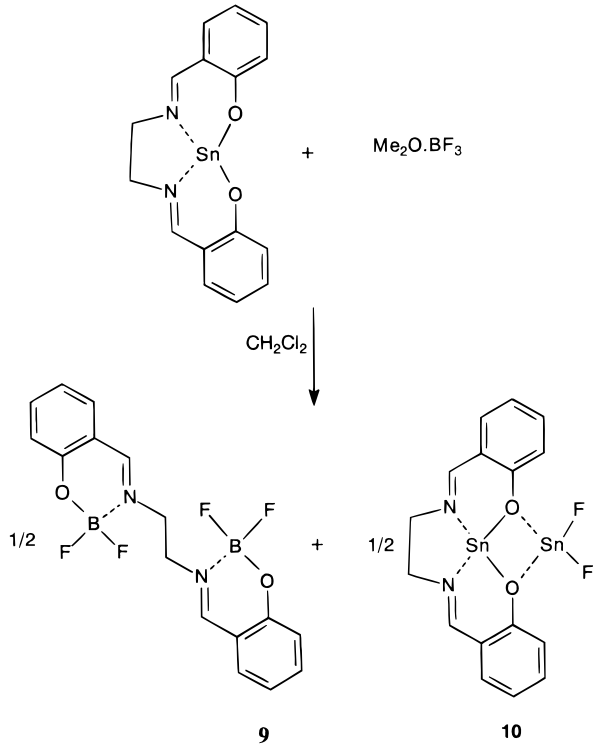
Scheme 5



9 **10**

pound $F_2B(Salen)FB_2$ (**9**), soluble in CH_2Cl_2, isolated in 90% yield as a yellow, amorphous solid (Scheme 5). Compound **9** probably has a structure similar to those of the known diborate salen derivatives $(RO)_2B(Salen)B(OR)_2$, in which a nitrogen of the salen group interacts with a boron center.[3n]

The BF_2 groups of **9** appeared as a triplet at −5.49 ppm ($^1J_{B-F}$ = 16.5 Hz) in the ^{11}B NMR spectrum and as two quartets at −62.70 and −61.47 ppm in the ^{19}F NMR spectrum. It is noteworthy that the salen compounds of the group 13 elements are primarily monometallic (see ref 3m,n and references therein).

Interaction of the $(L^2)M$ Species 2 or 3 with the Phosphorus Halides *t*-BuPCl$_2$, PCl$_3$, and(Y)PCl$_3$. In the search for new types of functionalized phosphines we extended this study to phosphorus halides.

Three reaction types were observed, depending on the nature of the phosphorus compound. Under mild conditions reactions of the tricoordinate phosphorus chlorides *t*-BuPCl$_2$ and PCl$_3$ with $(L^2)M$ afforded the phosphonite *t*-BuP(L^2) (**11**) and the phosphocations $[(L^2)P]^+$ in $[(L^2)P]^+[MCl_3]^-$ (**12**), respectively, while the tetracoordinate phosphoryl and thiophosphoryl chlorides gave the dinuclear dimeric phosphonates **13** and **14** (Scheme 6).

Compounds **11**−**14** were characterized by ^1H and ^{31}P NMR and FAB mass spectroscopy (in negative and positive modes for **12**). The δ value of the ^{31}P signal at 23 ppm of **12** is consistent with the phosphenium structure;[18] the ^1H NMR spectrum also testifies to the existence of N···P intramolecular coordinations in this molecule.

To our knowledge, this synthetic approach to the Salen phosphorus compounds has not been described previously. We have tried alternative routes to prepare these derivatives, but all resulted in mixtures of linear mononuclear and cyclic dinuclear species and the expected compounds, which could not be isolated in the pure state (Scheme 7).

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk and high-vacuum-line techniques. Dry, oxygen-free solvents were employed throughout. Solvents were distilled from sodium benzophenone or P_2O_5 before use. ^1H NMR spectra were recorded on a Bruker AC 80 spectrometer operating at 80 MHz (chemical shifts are reported in ppm relative to internal Me_4Si) and ^{13}C spectra on a AC 200 MHz spectrometer; the multiplicity of the ^{13}C NMR signals was determined by the APT technique. ^{19}F, ^{31}P, and ^{11}B NMR spectra were recorded on Bruker AC 200 and 400 MHz instruments. ^1H-decoupled ^{119}Sn NMR spectra were recorded on Bruker AC 200 and 400 MHz instruments (chemical shifts are reported in ppm relative to external Me_4Sn). Mass spectra under electron impact (EI) conditions at 70 and 30 eV were obtained on Hewlett-Packard 5989 and Nermag R10-10H spectrometers. FAB spectra were performed at the Service Commun de Spectrométrie de Masse de l'Université Paul Sabatier. IR and UV spectra were recorded on Perkin-Elmer 1600 FT-IR and Lambda-17 spectrophotometers. Melting points (uncorrected) were taken on a Leitz Biomed hot-plate microscope apparatus. Elemental analyses (C, H, N) were performed at the "Microanalysis Laboratory of the Ecole Nationale Supérieure de Chimie de Toulouse".

Reaction of (Salen)M (M = Ge, Sn) with $TiCl_4$. A dichloromethane solution of $TiCl_4$ (0.94 mL of a 1 M solution) (0.94 mmol) was added slowly with stirring to a solution of (Salen)M (M = Ge (**1**), Sn (**2**); 0.94 mmol) in CH_2Cl_2 (10 mL). Immediately, the solution became red and a precipitate appeared. After the solution had been stirred for 1 h, the solvent was removed in vacuo, the crude product was treated with pentane, and the resulting suspension was filtered. Compound **4** (**4a** or **4b**) was isolated as a red-orange powder. Yield: **4a,** 0.4 g, 82%; **4b**, 0.43 g, 80%. **4a**: mp >300 °C dec; ^1H NMR (DMSO-d_6) δ 4.16 (m, 4H, CH_2) 6.51−8.31 (m, 8H, Ar), 8.87 (s, 2H, CH=N); ^{13}C NMR (DMSO-d_6) δ 58.03 (CH_2), 114.86 (CH_{Ar}), 114.86 (CH_{Ar}), 116.19 (CH_{Ar}), 118.72 (CH_{Ar}), 122.16 (C_q), 122.82 (C_q), 134.31 (CH_{Ar}), 135.23 (CH_{Ar}), 161.24 (C−O), 162.41 (C−O), 161.99 (CH=N), 164.07 (CH=N); MS (FAB, glycerol) *m*/*z* 179 $[GeCl_3]^-$, 349 $[(Salen)TiCl]^+$. Anal. Calcd for $C_{16}H_{14}N_2O_2GeTiCl_4$: C, 36.47; H, 2.66; N, 5.32. Found: C, 35.95; H, 2.84; N, 5.18. **4b**: $^{119}Sn\{^1H\}$ NMR (DMSO-d_6) δ −613. MS (FAB, glycerol) *m*/*z* 225 $[SnCl_3]^-$, 349 $[(Salen)TiCl]^+$. Anal. Calcd for $C_{16}H_{14}N_2O_2SnTiCl_4$: C, 33.46; H, 2.46; N, 4.88. Found: C, 33.62; H, 2.63; N, 4.70.

Reaction of 3 with $TiCl_4$. In a similar manner, the reaction of **3** (0.71 g, 0.94 mmol) with $TiCl_4$ (0.94 mmol) in 10 mL of CH_2Cl_2 afforded **4c** (0.65 g, 74%). **4c**: mp >300 °C dec;

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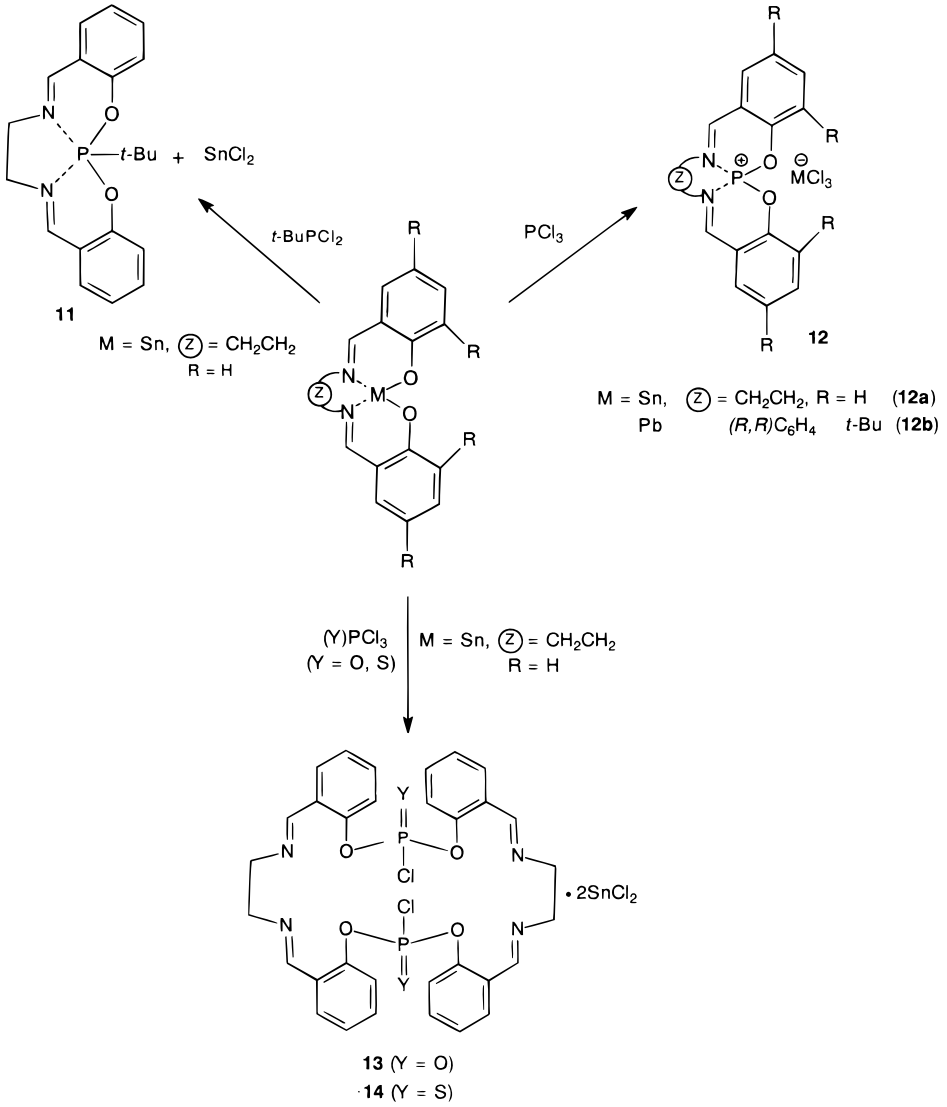
Scheme 6



^{1}H NMR (DMSO-d_6) δ 1.55 (s, 18H, *t*-Bu), 1.78 (s, 18H, *t*-Bu), 1.63−2.56 (m, 8H, CH_2), 3.43−3.85(m, 2H, CH), 7.25 (m, 2H, Ar), 7.76 (m, 2H, Ar), 8.45 (s, 2H, CH═N); MS (FAB, glycerol) *m*/*z* 313 $[PbCl_3]^-$, 627 $[(C_{36}H_{52}N_2O_2)TiCl]^+$. Anal. Calcd for $C_{36}H_{52}N_2O_2PbTiCl_4$: C, 45.96; H, 5.53; N, 2.98. Found: C, 46.43; H, 5.68; N, 2.83.

Reaction of (Salen)Sn with Cp_2TiCl_2. A solution of Cp_2TiCl_2 (0.18 g, 0.73 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of (Salen)Sn (0.28 g, 0.73 mmol) in CH_2Cl_2 (10 mL). The reaction mixture turned to red. A mass spectrum (FAB) of a sample of this solution exhibited a prominent peak at *m*/*z* 634 believed to correspond to the adduct ion [**6** + H]$^+$. After the solution had been stirred for 3 h at room temperature, the solvent was removed under reduced pressure and the residue washed with pentane. After filtration and drying in vacuo, ^{1}H NMR analysis of the crude product showed it to be a mixture of **5** (∼60%) and CpSnCl (∼40%). Purification of this mixture by crystallization from a variety of solvents (toluene,THF, pentane) permitted the elimination of a major quantity of CpSnCl (**14**). **5**: mp >300 °C dec; ^{1}H NMR ($CDCl_3$) δ 4.09 (m, 4H, CH_2), 6.37 (s, 5H, Cp), 6.42−7.90 (m, 8H, Ar), 8.74 (s, 2H, CH═N). CpSnCl: MS *m*/*z* 220 $[CpSnCl]^{\bullet+}$, 185 $[CpSn]^+$, 155 $[SnCl]^+$.

Reaction of (Salen)Sn with $NiCl_2$·DPPE. A solution of $NiCl_2$·DPPE (0.25 g, 0.47 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a solution of (Salen)Sn (0.18 g, 0.47 mmol) in 10 mL of CH_2Cl_2. After the reaction mixture was stirred for 2 h at room temperature, the solvent was removed under reduced pressure and the red brown residual solid was treated with pentane. The resulting suspension was filtered, and the collected solid was dried in vacuo to afford **7** (0.23 g, 96%) as a red-brown powder. **7**: ^{1}H NMR (DMSO-d_6) δ 3.42 (m, 4H, CH_2), 6.40−7.40 (m, 8H, Ar), 7.88 (s, 2H, CH═N); ^{13}C NMR (DMSO-d_6) δ 57.91 (CH_2), 114.23 (CH_{Ar}), 119.89 (CH_{Ar}), 120.26 (C_q), 132.71 (C_q), 133.36 (CH_{Ar}), 163.84 (C−O), 162.54 (CH═N); ^{119}Sn{^{1}H} NMR (DMSO-d_6) δ −334; MS *m*/*z* 324 [Ni(Salen)]. Anal. Calcd for $C_{16}H_{14}N_2O_2SnNiCl_2$: C, 37.36; H, 2.75; N, 5.45. Found: C, 37.51; H, 2.91; N, 5.32.

After 1 week, a DMSO solution of the complex **7** led to crystals of Ni(Salen).[17]

Reaction of (Salen)Sn with $SnCl_2$. A suspension of $SnCl_2$ (0.0.9 g, 0.47 mmol) in 5 mL of CH_2Cl_2 was added slowly to a solution of (Salen)Sn (0.18 g, 0.47 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred for 3 h at room temperature. A pale yellow precipitate appeared. Filtration, washing with pentane, and removal of the solvent under reduced pressure afforded **8** as a pale yellow solid (0.25 g, 95%). **8**: mp >300 °C dec; ^{1}H NMR (DMSO-d_6) δ 3.91 (m, 4H, CH_2), 6.60−7.50 (m, 8H, Ar), 8.39 (s, 2H, CH═N); ^{13}C NMR (DMSO-d_6) δ 58.03 (CH_2), 114.86 (CH_{Ar}), 114.86 (CH_{Ar}), 116.19 (CH_{Ar}), 118.72 (CH_{Ar}), 122.16 (C_q), 122.82 (C_q), 134.31 (CH_{Ar}), 135.23 (CH_{Ar}), 161.24 (C−O), 162.41 (C−O), 161.99 (CH═N), 164.07 (CH═N); ^{119}Sn{^{1}H} NMR (DMSO-d_6) δ −336 ($SnCl_2$), −554 [Sn-

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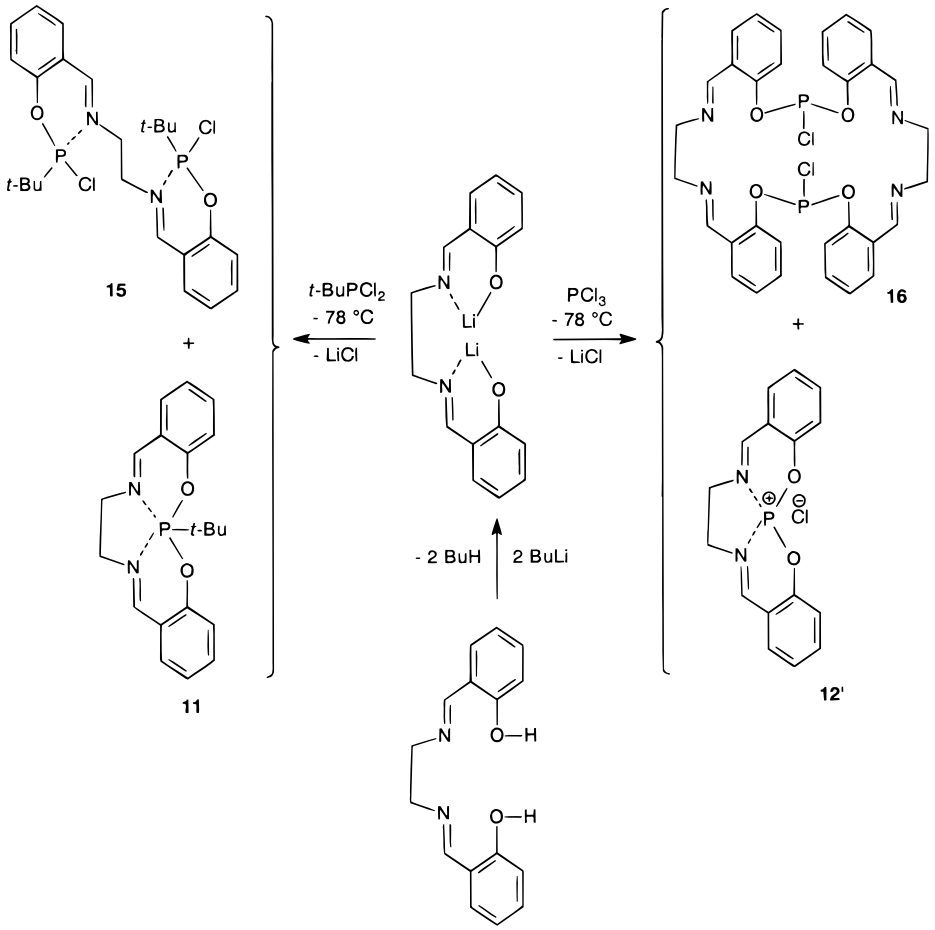
Scheme 7



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(Salen)]; MS *m*/*z* 386 [Sn(Salen)]$^{\bullet+}$. Anal. Calcd for $C_{16}H_{14}N_2O_2Sn_2Cl_2$: C, 33.34; H, 2.45; N, 4.86. Found: C, 33.45; H, 2.59; N, 4.71.

Reaction of (Salen)Sn with BF_3·Me_2O. BF_3·Me_2O (62 μL, 0.67 mmol) was added slowly to a solution of (Salen)Sn (0.26 g, 0.67 mmol) in 10 mL of CH_2Cl_2. The resulting yellow suspension was filtered, and (Salen)Sn·SnF_2 (**10**) was isolated as a yellow solid (0.17 g, 92%). Evaporation of the filtrate in vacuo yielded BF_2(Salen)BF_2 (**9**) as a bright yellow-orange powder (0.11 g, 89%). **10**: ^{1}H NMR (DMSO-d_6) δ 3.92 (s, 4H, CH_2), 6.50−7.70 (m, 8H, Ar), 8.42 (s, 1H, CH=N); ^{13}C NMR (DMSO-d_6) δ 58.03 (CH_2), 114.86 (CH_{Ar}), 114.86 (CH_{Ar}), 116.19 (CH_{Ar}), 118.72 (CH_{Ar}), 122.16 (C_q), 122.82 (C_q), 134.31 (CH_{Ar}), 135.23 (CH_{Ar}), 161.24 (C−O), 162.41 (C−O), 161.99 (CH=N), 164.07 (CH=N); ^{19}F NMR ($CDCl_3$) δ −72.48 (s, $^1J_{Sn-F}$ = 2122 Hz); ^{119}Sn{^{1}H} NMR (DMSO-d_6) δ −664 (t, SnF_2), −702 [br, Sn(Salen)]; MS *m*/*z* 386 [Sn(Salen)]$^{\bullet+}$. Anal. Calcd for $C_{16}H_{14}N_2O_2Sn_2F_2$: C, 35.30; H, 2.59; N, 5.15. Found: C, 35.62; H, 2.63; N, 4.92. **9**: ^{1}H NMR (DMSO-d_6) δ 4.02 (m, 4H, CH_2) 6.43−8.22 (m, 8H, Ar), 8.42 (s, 2H, CH=N); ^{11}B NMR (DMSO-d_6) δ −5.49 (t, BF_2); ^{19}F NMR (DMSO-d_6) δ −62.70, −61.47 (q, BF_2, $^1J_{B-F}$ = 16.5 Hz); MS *m*/*z* 364 [(Salen)$(BF_2)_2$]$^{\bullet+}$, 296 [M − BF_3]$^+$. Anal. Calcd for $C_{16}H_{14}N_2O_2B_2F_4$: C, 52.73; H, 3.87; N, 7.69. Found: C, 52.86; H, 4.01; N, 7.50.

Reaction of (Salen)Sn with *t*-BuPCl$_2$. A solution of *t*-BuPCl$_2$ (0.04 g, 0.26 mmol) in 5 mL of CH_2Cl_2 was added at room temperature to a solution of (Salen)Sn (0.10 g, 0.26 mmol) in 10 mL of CH_2Cl_2. After 2 h of stirring at room temperature, the solvent was removed under reduced pressure, and the residue was treated with pentane. By filtration and drying in vacuo, **11** was obtained as a bright yellow powder (0.07 g, 82%). **11**: ^{1}H NMR ($CDCl_3$) δ 0.5−1.4 (m, 9H, *t*-Bu), 4.08 (m, 4H, CH_2), 6.40−7.50 (m, 8H, Ar), 8.40 (s, 2H, CH=N); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 77.9; MS *m*/*z* 297 [M − *t*-Bu]$^+$. Anal. Calcd for $C_{20}H_{23}N_2O_2P$: C, 67.77; H, 6.55; N, 7.91. Found: C, 67.91; H, 6.70; N, 7.80.

Reaction of (Salen)Sn with PCl_3. A solution of (Salen)Sn (0.18 g, 0.47 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of PCl_3 (0.04 mL, 0.47 mmol) in CH_2Cl_2 (5 mL). A yellow precipitate was immediately formed. Filtration, washing with pentane, and drying in vacuo yielded **12a** as a pale yellow powder (0.23 g, 95%). **12a**: ^{1}H NMR (DMSO-d_6) δ 3.80 (m, 4H, CH_2), 6.50−7.70 (m, 8H, Ar), 8.05 (s, 2H, CH=N); ^{31}P NMR (DMSO-d_6) δ 23; ^{119}Sn{^{1}H} NMR (DMSO-d_6) δ −613; MS (FAB, glycerol) *m*/*z* 225 [$SnCl_3$]$^-$, 297 [(Salen)P]$^+$. Anal. Calcd for $C_{16}H_{14}N_2O_2SnPCl_3$: C, 36.79; H, 2.70; N, 5.37. Found: C, 36.86; H, 2.82; N, 5.20.

Reaction of 3 with PCl_3. Using the same operating conditions as in the previous preparation, **12b** was obtained from **3** (0.35 g, 0.47 mmol) and PCl_3 (0.04 mL, 0.47 mmol). Yield: 0.2 g (49%). **12b**: ^{1}H NMR (DMSO-d_6) δ 1.54 (s, 18H, *t*-Bu), 1.76 (s, 18H, *t*-Bu), 1.63−2.56 (m, 8H, CH_2), 3.42−3.85 (m, 2H, CH), 7.25 (m, 2H, Ar), 7.76 (m, 2H, Ar), 8.45 (s, 2H, CH=N); ^{31}P NMR (DMSO-d_6) δ 23.54; MS (FAB, glycerol) *m*/*z* 313 [$PbCl_3$]$^-$, 575 [$(C_{36}H_{52}N_2O_2)P$]$^+$. Anal. Calcd for $C_{36}H_{52}N_2O_2PbPCl_3$: C, 48.65; H, 5.86; N, 3.15. Found: C, 49.18; H, 6.12; N, 3.04.

Reaction of (Salen)Sn with O=PCl_3. To a solution of (Salen)Sn (0.26 g, 0.67 mmol) in 10 mL of CH_2Cl_2 was added dropwise phosphoryl chloride (0.10 g, 0.67 mmol). A yellow precipitate immediately appeared. Following a procedure similar to that for **12a**, **13** (0.59 g, 82%) was isolated. **13**: ^{1}H NMR (DMSO-d_6) δ 4.04 (m, 4H, CH_2), 6.50−7.70 (m, 8H, Ar), 8.09 (s, 2H, CH=N); ^{31}P NMR (DMSO-d_6) δ −8.90; ^{119}Sn{^{1}H} NMR (DMSO-d_6) δ −110; MS (FAB, glycerol) *m*/*z* 696 [(Salen)P(O)Cl]$_2$. Anal. Calcd for $C_{32}H_{28}N_4O_6Sn_2P_2Cl_6$: C, 35.70; H, 2.62; N, 5.21. Found: C, 35.92; H, 2.75; N, 5.12.

Reaction of (Salen)Sn with S=PCl_3. Thiophosphoryl

chloride (82 μL, 0.67 mmol) was added dropwise to a solution of (Salen)Sn (0.26 g, 0.67 mmol) in CH_2Cl_2 (10 mL). The resulting suspension was stirred for 2 h at room temperature. **14** was isolated as a pale orange powder (0.62 g, 84%) in a way similar to that for **12a**. **14**: ^{1}H NMR (DMSO-d_6) δ 4.22 (m, 4H, CH_2), 6.70−7.70 (m, 8H, Ar), 8.15 (s, 2H, CH═N); ^{31}P NMR (DMSO-d_6) δ 63.2; ^{119}Sn{^{1}H} NMR (DMSO-d_6) δ −111; MS (FAB, glycerol) *m*/*z* 728 [(Salen)P(S)Cl]$_2$. Anal. Calcd for $C_{32}H_{28}N_4O_4S_2Sn_2P_2Cl_6$: C, 34.67; H, 2.55; N, 5.06. Found: C, 34.90; H, 2.63; N, 4.92.

Reaction of (Salen)Li$_2$ with *t*-BuPCl$_2$. A solution of BuLi (8 mmol, 5 mL of a 1.6 M solution in hexane) was added dropwise to a solution of (Salen)H_2 (1.07 g, 4 mmol) in THF (30 mL). The resulting solution was stirred for 2 h at room temperature, cooled to ca. −78 °C with constant stirring, and added dropwise to *t*-BuPCl$_2$ (0.63 g, 4 mmol) in THF (20 mL) at ca. −78 °C. The reaction mixture was stirred for 30 min at ca. −78 °C and for an another 2 h upon warming to room temperature. The volatile materials were removed under reduced pressure. Addition of pentane (20 mL), filtration, and concentration of the filtrate gave a mixture of **11** (10%) and **15** (90%) (by ^{31}P NMR spectroscopy) as a yellow solid. All attempts of separation of these products by crystallization from various solvents (toluene, THF, pentane) failed. **15**: ^{1}H NMR ($CDCl_3$) δ 0.3−1.4 (m, 18H, *t*-Bu), 3.90 (m, 4H, CH_2), 6.60−7.50 (m, 8H, Ar), 8.32 (s, 2H, CH═N); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 165.

Reaction of (Salen)Li$_2$ with PCl$_3$. The first step of the procedure is completely analogous to that described above using (Salen)Li_2 (4 mmol; obtained from BuLi (5 mL of 1.6 M in hexane, 8 mmol) and (Salen)H_2 (1.07 g, 4 mmol)) and PCl_3 (0.35 mL, 4 mmol). Filtration of the reaction mixture afforded **12′** (0.39 g, 30%) as a yellow solid. The filtrate was concentrated under reduced pressure, and the residue was treated with toluene (20 mL). After filtration, the concentration of the remaining solution in vacuo afforded **16** (0.92 g, 70%). **12′**: ^{1}H NMR (DMSO-d_6) δ 4.38 (m, 4H, CH_2), 6.80−7.50 (m, 8H, Ar), 8.12 (s, 2H, CH═N); ^{31}P NMR (DMSO-d_6) δ 23; MS (FAB, glycerol) *m*/*z* 35 [Cl]$^-$, 297 [(Salen)P]$^+$. **16**: ^{1}H NMR ($CDCl_3$) δ 3.81 (m, 4H, CH_2), 6.52−7.74 (m, 8H, Ar), 8.06 (s, 2H, CH═N); ^{31}P NMR ($CDCl_3$) δ 146.

X-ray Crystal Data for 3: $C_{36}H_{52}N_2O_2Pb$, M_r = 751.99, tetragonal, $P4_1$, $a = b$ = 13.9282(6) Å, c = 17.7840(8) Å, V = 3450.0(3) Å^3, Z = 4, ρ_c = 1.448 Mg m^{-3}, $F(000)$ = 1520, λ = 0.710 73 Å, T = 193(2) K, μ(Mo Kα) = 4.922 mm^{-1}, crystal size 0.4 × 0.05 × 0.05 mm, 1.86° < θ < 24.70°. A total of 38 808 reflections (5883 independent, R_{int} = 0.0883) were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer. A semiempirical absorption correction was employed[19] (T_{min} = 0.716 952, T_{max} = 1.000 000). The structure was solved by direct methods (SHELXS-97),[20] and 338 parameters were refined using the least-squares method on F^2.[21] The largest electron density residue was 2.404 e Å^{-3}. R1 (for $F > 2\sigma(F)$) = 0.0662, and wR2 = 0.1583 (all data), with R1 = $\sum||F_o| - |F_c||/\sum|F_o|$ and wR2 = $(\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$.

Supporting Information Available: Tables giving full details of the crystallographic data and data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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