Structure Investigations of Group 13 Derivatives of *N*-Phenylsalicylideneimine

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Received May 5, 2003

The reaction of MMe_3 with 1 molar equiv of *N*-phenylsalicylideneimine (HsaldPh) yields the O,N-chelate complexes $Me_2M(saldPh)$ (where M = Al (**1**), Ga (**2**), In (**3**)) in high yields. The reaction of **1** with γ-picoline results in a ligand redistribution reaction and the formation of the five-coordinate complex $MeAl(saldPh)_2$ (**4**), while the gallium and indium compounds are stable in the presence of γ-picoline. The resulting compounds have been characterized in a solution by NMR and IR spectroscopy and cryoscopic molecular weight measurements, and their molecular and crystal structure have been determined by X-ray crystallography. Compounds **1** and **2** exist as monomeric tetrahedral complexes, while the indium analogue **3** is dimeric with the $In_2(\mu\text{-}O)_2$ bridges and five-coordinate metal centers. The five-coordinate methylaluminum compound **4** exhibits trigonal-bipyramidal geometry of the metal center. The obtained results show that a Schiff base acts as a strongly coordinating chelate ligand and, in this regard, it resembles the symmetrical acetylacetonato ligand and related β-diketonates. An extended crystal structure analysis reveals that the isostructural crystalline complexes **1** and **2** comprise monomeric four-coordinate molecules linked by $C{-}H_{imino}\cdots O$ hydrogen bonds, forming helical chains. Parallel left- and right-handed helices joined by $C{-}H\cdots\pi$ interactions give rise to the 3D extended tetragonal framework, with voids filled by solvent molecules. In the crystalline complex **4** the $C{-}H_{aryl}\cdots O$ hydrogen bonds organize molecules into H-bonded dimers.

Introduction

Metal complexes of monoanionic, both bidentate and pendant arm multidentate Schiff bases and related dianionic ligands such as Salen (ethylenediamine bridged) and Salophen (*o*-phenylenediamine-bridged) have played a very important role in the development of coordination chemistry for decades.[1] In Schiff base complexes, the coordination environment at the metal center can be modified by attaching different substituents to the ligand, which provides a useful range of steric and electronic properties essential for the fine tuning of structure and reactivity. Therefore, it is also not surprising that both transition-metal and p-block-metal derivatives of Schiff bases have been shown to catalyze a wide variety of reactions.[2,3] For example, aluminum-based complexes, which are of particular relevance to this paper, have been used as catalysts in the polymerization of ethylene[4] and methacrylate[5] and the ring-opening polymerization of heterocyclic monomers.[6] The chemistry of group 13 Salen and Salophen derivatives has been reviewed by Atwood recently.[1] We have been attracted to the study of bidentate Schiff base ligands in the course of our investigation on the molecular architecture, bonding, and reactivity of group 13 metal chelate complexes,[7] specifically in studies of the role of the bidentate ligand nature and interplay of coordinative bonds and hydrogen bonds.[7b,8,9] We assumed also that this group of complexes should be a good basic

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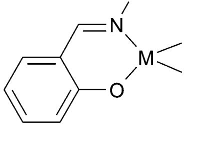
10.1021/om030331v CCC: $25.00

model system for the study of the role of hydrogen bonding on the structure of Schiff base metal complexes. Additionally, our choice of target complexes was dictated by the fact that the organometallic chemistry of group 13 elements with bidentate salicylideneiminate ligands remains relatively poorly explored (for example, the structurally characterized four-coordinated aluminum complexes of this type include only sterically encumbered ligands,[10,11] while complexes incorporating boron and gallium have been rare[12−14]), and these studies are in the course of our recent investigations toward volatile main-group organometallic compounds as precursors for MOCVD.[15,16]

Our previous studies on the solid-state and solution properties of various group 13 chelate complexes have revealed that minor differences in the subunit structure can have a profound effect on the association of metal alkoxides (aryloxides).[7b,17] We have delineated factors which provide a better understanding of the structural and bonding parameters for the metal alkyl derivatives of saturated and unsaturated donor-functionalized hydroxy compounds (L−H) upon moving from monomeric four-coordinate $R_2M(\eta^2\text{-L})$ to five-coordinate $[R_2M(\mu,\eta^2\text{-L})]_2$ complexes or from four-coordinate $[R_2M(\mu,\eta^1\text{-L})]_2$ to five-coordinate $[R_2M(\mu,\eta^2\text{-L})]_2$ adducts.[7c,18,19] Very recently, we have also reported results aiding our understanding of relationships between intra- and intermolecular forces resulting from donor−acceptor and hydrogen-bonding interactions using group 13 alkoxides and carboxylates as model complexes.[7b,9] In a continuation of our systematic studies, we report here on structure investigations of the group 13 organometallic chelate complexes (M = Al, Ga, In) with salicylideneiminate anion as the O,N-bidentate ligand. The influence of weak hydrogen bonds on the supramolecular structure of resulting complexes is also discussed.

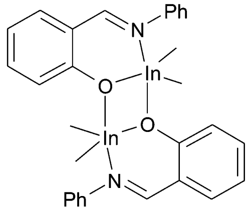
Results and Discussion

Synthesis and Solution Structure. The reaction of Me_3M with 1 equiv of *N*-phenylsalicylideneimine (saldPh-H) in toluene solution allows for the isolation of the chelate complexes Me_2M(saldPh) (where M = Al (**1**), Ga (**2**), In (**3**)) almost quantitatively. Each compound was isolated as a yellow crystalline solid following evaporation to dryness of the reaction mixture and subsequent recrystallization from hexane/CH_2Cl_2 solution at 0 °C. The resulting compounds have been characterized in a solution by NMR and IR spectroscopy and cryoscopic molecular weight measurements. In the solid state, the molecular structures of **1**−**3** have been determined by X-ray diffraction techniques. The molecular weight measurements have revealed that the aluminum and gallium compounds **1** and **2** occur as monomeric species in solution. Interestingly, a freshly prepared benzene solution of the crystalline **2** consists of some higher aggregated species, as judged from the cryoscopic determination, likely the hydrogen-bonded associates (vide infra). Initially, the degree of association varied in the range of 1.2−1.3 and after ca. $^1/_2$ h reached a value of 1.0, corresponding to monomeric species (see Experimental Section). In contrast, the indium compound **3** occurs as a dimer in benzene solution. The ^{27}Al NMR spectrum of **1** consists of a single resonance at 149 ppm corresponding to a four-coordinate aluminum center. It is worth noting that the intensity of the resonance signal is relatively low and a problem with the detection of resonance signals presumably results from the quadrupole moment of aluminum and nitrogen (this aspect will be discussed in more details elsewhere). The ^{1}H NMR spectra of **1**−**3** show no complexity, and single resonances of the M−Me protons as well as the N=CH proton and multiplets of aromatic protons are observed. Thus, the above data are consistent with the monomeric tetrahedral chelate structure **I** for the aluminum and gallium derivatives and dimeric structure **II** for the indium complex.



M = Al (**1**) or Ga (**2**)

I



II

Ligand Redistribution Reactions. We have previously reported that four-coordinate dialkylaluminum complexes with a symmetrical bidentate acetylacetonate ligand disproportionate in the presence of a Lewis base, and the formation of stable five-coordinate adducts with Lewis bases, i.e. $R_2Al(acac)(L)$, or bis-chelate $RAl(acac)_2$ complexes (as an intermediate in the disproportionation reaction) was not observed.[20,21] We have been able to isolate analogous five-coordinate aluminum complexes, however, for unsymmetrical bidentate ligands such as

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methyl salicylate (mesalH) or 2′-aminoacetophenone (amketH).[22,23] As an extension of our studies on the reactivity of group 13 chelate complexes toward nucleophilic reagents and ligand redistribution reactions we have investigated the reaction of $Me_2M(saldPh)$ with γ-picoline. The reaction of **1** with 1 equiv (or excess) of γ-picoline in toluene solution at ambient temperature resulted in a disproportionation reaction and the formation of the five-coordinate complex $MeAl(saldPh)_2$ (**4**) almost quantitatively. The ^{27}Al NMR spectrum of **4** consists of a single resonance at 57 ppm corresponding to the five-coordinate aluminum center.[24] It is interesting to note at this point that the chemical shift of **4** is close to those observed for the related O,N-chelate complex $MeAl(amket)_2$ (67 ppm)[23] and O,O′-chelate complex $MeAl(mesal)_2$ (66 ppm).[24] Thus, for the $RAl(O,N)_2$ complexes the chemical shifts fall in a relatively narrow range, ~10 ppm, despite the reverse position of N and O substituents in the metal coordination sphere (the equatorial vs axial position) or substitution of N- for O-donor sites. These observations indicate that the nature of a chelating ligand in the neutral five-coordinated alkylaluminum bis-chelate complexes does not affect substantially the aluminum nuclei shielding. In contrast to the aluminum complex **1**, the gallium and indium analogues are stable in the presence of γ-picoline, which clearly demonstrates that the latter compounds are much less prone toward ligand redistributions. There is also no detectable complexation of γ-picoline by the metal center of **2** and **4** by ^1H NMR spectroscopy.

Solid-State Structures of 1−4. The X-ray diffraction studies were carried out in order to determine the degree of aggregation, the presence or absence of intermolecular noncovalent interactions, and other pertinent structural details. Crystals of compounds **1**−**3** suitable for an X-ray structure determination were grown from toluene/*n*-hexane solutions at −20 °C. The solid structures of **1** and **2** are isostructural and comprise monomeric species with the extended hydrogen bond network. Compound **3** is dimeric in the solid state, with no unusually short intermolecular contacts. Compounds **1** and **2** both crystallize in the tetragonal space group $I4_1/a$ as solvates with disordered molecules of *n*-hexane. The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively, while selected interatomic distances and angles are collected in Table 1. Both compounds exist in the solid state as monomeric four-coordinate chelate complexes. The chelate ligands bind to the metal centers in an unsymmetrical fashion. The Al(1)−O(1) and much longer Al(1)−N(1) distances for **1** (1.7724(19) and 1.963(2) Å) are in accordance with corresponding linkages in the simple four-coordinate chelate analogues (Schiff base derivatives).

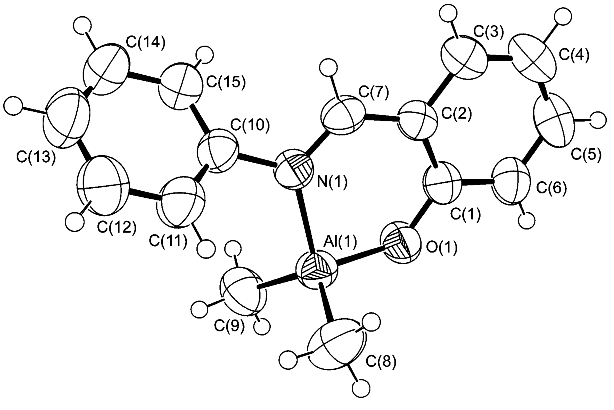

Figure 1. ORTEP diagram of $Me_2Al(saldPh)$ (**1**). Thermal ellipsoids are drawn at 50% probability.

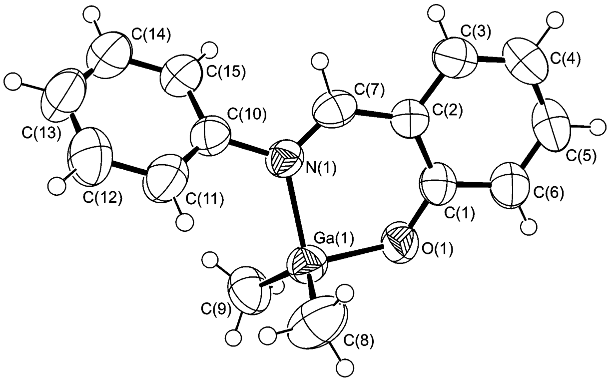

Figure 2. ORTEP diagram of $Me_2Ga(saldPh)$ (**2**). Thermal ellipsoids are drawn at 50% probability.

In compound **2** the Ga(1)−O(1) distance (1.889(3) Å) is longer by about 0.12 Å than that found for **1**. However, the Ga−C bond lengths are the same as the Al−C lengths. Taking into account the differences between the covalent or ionic radii of aluminum (1.18, 0.53 Å) and gallium (1.26, 0.61 Å), one should state the relative weakening of M−O and strengthening of M−C bonds on going from aluminum to gallium: e.g., the increase of covalent character of M−C bonds. It is consistent with the increasing electronegativity of the metal centers and indicates greater s-orbital character in the Ga−C bonds. In both structures, the metal center has a distorted-tetrahedral geometry with angles ranging from 95.14(9) to 119.09(14)° and from 93.19(14) to 125.3(3)° in **1** and **2**, respectively. The most acute angle in each case is associated with the bite of the chelating ligand. Consequently, the greater s-orbital character of Ga−C bonds leads to a more obtuse C−Ga−C angle (125.3(3)°) by comparison to the C−Al−C angle (119.09(14)°). The same trend in widening of the C−M−C angle has been observed for the dimeric five-coordinate $[R_2M(O,O')]_2$ -type complexes when passing from Al to Ga and In derivatives (vide infra).[7a] The remaining bond lengths and angles of the O,N-ligands in compounds **1** and **2** do not differ significantly. The six-membered chelate rings in compounds **1** and **2** adopt a sofa conformation. The Al and Ga atoms are displaced by 0.250(3) and 0.314(5) Å, respectively, out of the almost flat ligand plane. We demonstrated recently that for unsaturated bidentate ligands the strength of the interaction between donor sites and the metal center is significantly controlled by the conformation of the

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(21) It is interesting to note that there has been one report on the isolation and structure characterization of a five-coordinate dimethylgallium complex with a related symmetrical ligand, $Me_2Ga(hfac)(L)$ (where hfac = 1,1,1,5,5,5-hexafluoro-2,4-penatedionato and L = pyridine): Beachley, O. T., Jr.; Gardinier, J. R.; Churchill, M. R.; Toomey, L. M. *Organometallics* **1998**, *17*, 1101−1108.

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Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for Compounds 1−4

1·$^1/_4$C$_6$H$_{14}$		**2**·$^1/_4$C$_6$H$_{14}$	
Al(1)−O(1)	1.7724(19)	Ga(1)−O(1)	1.889(3)
Al(1)−N(1)	1.963(2)	Ga(1)−N(1)	2.023(3)
Al(1)−C(8)	1.943(3)	Ga(1)−C(8)	1.942(5)
Al(1)−C(9)	1.946(3)	Ga(1)−C(9)	1.940(5)
O(1)−C(1)	1.337(3)	O(1)−C(1)	1.324(5)
N(1)−C(7)	1.296(3)	N(1)−C(7)	1.288(5)
C(1)−C(2)	1.402(3)	C(1)−C(2)	1.407(6)
C(2)−C(7)	1.434(3)	C(2)−C(7)	1.432(6)
C(8)−Al(1)−C(9)	119.09(14)	C(8)−Ga(1)−C(9)	125.2(3)
O(1)−Al(1)−N(1)	95.14(9)	O(1)−Ga(1)−N(1)	93.21(14)
C(1)−O(1)−Al(1)	129.71(17)	C(1)−O(1)−Ga(1)	127.1(3)
C(7)−N(1)−Al(1)	121.68(18)	C(7)−N(1)−Ga(1)	122.1(3)
O(1)−C(1)−C(2)	121.6(2)	O(1)−C(1)−C(2)	123.7(4)
C(1)−C(2)−C(7)	123.2(2)	C(1)−C(2)−C(7)	123.7(4)
N(1)−C(7)−C(2)	126.5(3)	N(1)−C(7)−C(2)	127.3(4)
Al(1)−O(1)−C(1)−C(2)	−13.4(4)	Ga(1)−O(1)−C(1)−C(2)	−15.5(7)
Al(1)−N(1)−C(7)−C(2)	0.7(4)	Ga(1)−N(1)−C(7)−C(2)	1.9(7)

3		**4**	
In(1)−O(1)	2.158(3)	Al(1)−O(1)	1.7725(11)
In(1)−N(1)	2.366(3)	Al(1)−O(2)	1.7771(11)
In(1)−O(1′)	2.477(3)	Al(1)−N(1)	2.1034(12)
In(1)−C(8)	2.137(5)	Al(1)−N(2)	2.1305(13)
In(1)−C(9)	2.133(5)	Al(1)−C(8)	1.9775(17)
O(1)−C(1)	1.331(5)	O(1)−C(1)	1.3277(17)
N(1)−C(7)	1.286(5)	O(2)−C(21)	1.3197(17)
C(1)−C(2)	1.409(6)	N(1)−C(7)	1.2869(19)
C(2)−C(7)	1.440(6)	N(2)−C(27)	1.2905(19)
C(9)−In(1)−C(8)	140.3(2)	O(1)−Al(1)−O(2)	118.49(6)
C(9)−In(1)−O(1)	110.58(16)	O(1)−Al(1)−C(8)	119.78(7)
C(8)−In(1)−O(1)	108.29(17)	O(2)−Al(1)−C(8)	121.72(7)
O(1)−In(1)−N(1)	82.01(11)	N(1)−Al(1)−N(2)	169.20(5)
O(1)−In(1)−O(1′)	74.51(11)	O(1)−Al(1)−N(1)	88.92(5)
N(1)−In(1)−O(1′)	156.23(11)	O(2)−Al(1)−N(2)	87.54(5)
C(1)−O(1)−In(1)	133.2(3)	C(1)−O(1)−Al(1)	133.70(10)
C(1)−O(1)−In(1′)	121.3(2)	C(21)−O(2)−Al(1)	134.48(9)
C(7)−N(1)−In(1)	125.1(3)	C(7)−N(1)−Al(1)	123.57(10)
In(1)−O(1)−In(1)	105.49(11)	C(27)−N(2)−Al(1)	122.02(10)
In(1)−O(1)−C(1)−C(2)	−4.8(6)	Al(1)−O(1)−C(1)−C(2)	19.7(2)
In(1)−N(1)−C(7)−C(2)	−13.5(6)	Al(1)−O(2)−C(21)−C(26)	−156.11(13)

chelate heterocyclic ring.[25] Hence**,** it is reasonable to assume that the conformation of the heterocyclic ring in **1** and **2**, in the absence of steric hindrances, results from the intermolecular noncovalent forces.

A detailed inspection of the crystal structures of compounds **1** and **2** revealed that the weak intermolecular hydrogen bond systems play a substantial role in the molecular assembly of crystalline complexes. Most interestingly, in both crystals adjacent monomeric moieties are linked by the C−H$_{imino}$···O hydrogen bonds (with the aryloxide oxygen acting as the hydrogen acceptor) to form an infinite 1D helix running along the *c* axis, as depicted in Figure 3a and Figure S1a (Supporting Information) for **1** and **2**, respectively. The helical structures of **1** and **2** deserve special attention. The helices are formed around crystallographic 4$_1$ and 4$_3$ screw axes, and each coil of the helix therefore contains four residues. The distances between coils are equal, ~20.0 Å, and correspond to the unit cell parameter *c* (19.995(3) and 20.0042(13) Å for **1** and **2**, respectively). Additionally, weaker interactions of the C−H···π(Ph) type between aromatic hydrogens and ligand aromatic rings of adjacent molecules significantly mediate the assembly. In both structures the intermolecular C−H···π-centroid separations are equal, ~3.03 Å, and lie in the accepted distance range for these types of contacts.[26] In crystals of **1** and **2** parallel alternating left- and right-handed helical chains are thus further joined by C−H···π(Ph) interactions to form a tetragonal net. In that case one could expect the formation of channels surrounded by parallel helices. However, examination of the space-filling model indicates only the existence of oblate spheroidal cavities with dimensions of ~7.2 × 6.5 Å into which the guest molecules (*n*-hexane) are included without any specific interaction between guest and host. The resulting H-bonded 3D frameworks with the disordered solvent molecules are

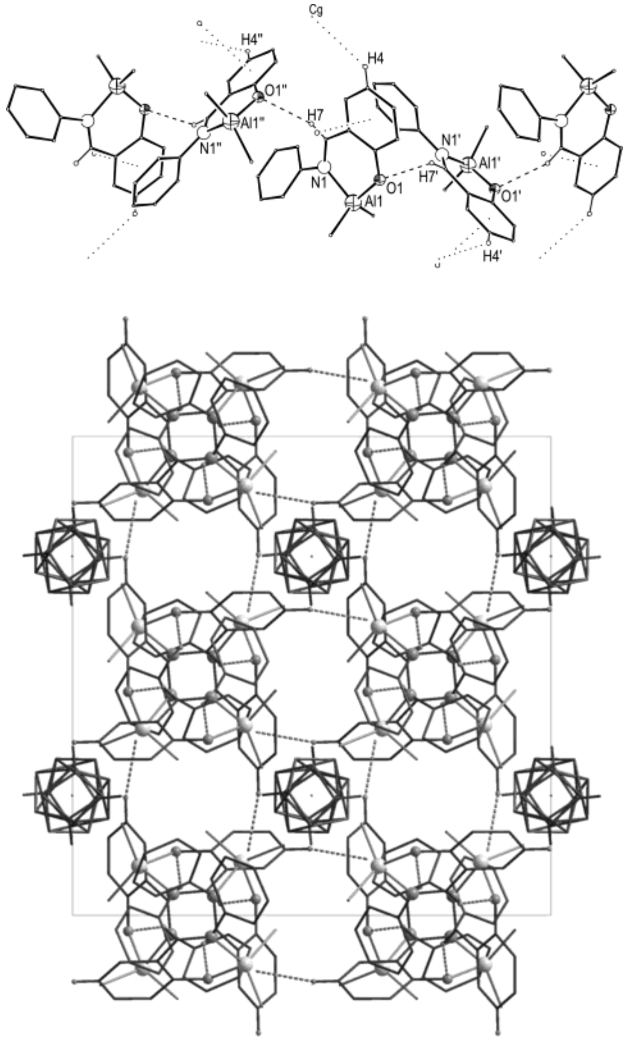

Figure 3. (a, top) View of the helical chain structure of Me$_2$Al(saldPh) (**1**). (b, bottom) View of the crystal packing in compound **1** along the *c* axis. The dashed lines and the dotted lines represent C−H···O and C−H···π(Ph) hydrogen bonds, respectively. Disordered *n*-hexane molecules are each shown as a superposition of four sets of atomic positions. Hydrogen atoms are omitted, excluding those involved in H-bond formation.

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[25] Lewiński, J.; Goś, P.; Kopeć, T.; Lipkowski, J.; Luboradzki, R. *Inorg. Chem. Commun.* **1999**, *2*, 374−377.

[26] Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; IUCr Monographs on Crystallography 9; Oxford University Press/International Union of Crystallography: Oxford, U.K., 1999.

Table 2. Selected Intra- and Intermolecular Contacts (Å, deg) in the Structures of 1, 2, and 4

C−H···O

compd		C−H (Å)	H···O (Å)	C···O (Å)	C−H···O (deg)
1	C(7)−H(7)···O(1′)[a]	0.93	2.54	3.327(3)	143
2	C(7)−H(7)···O(1′)[a]	0.93	2.51	3.302(5)	144
	C(14)−H(14)···O(1′)[b]	0.97(2)	2.60(2)	3.500(2)	153.9(16)
4	C(15)−H(15)···O(2′)[b]	0.94(2)	2.61(2)	3.456(2)	148.8(15)
	C(35)−H(35)···O(1)	0.97(2)	2.52(2)	3.049(2)	114.2(15)

C−H···π

		C−H (Å)	H···Cg (Å)[d]	C···Cg (Å)	C−H···Cg (deg)
1	C(4)−H(4)···π(Ph′)[c]	0.93	3.03	3.789(4)	140
2	C(4)−H(4)···π(Ph′)[c]	0.93	3.03	3.800(6)	142

[a] Symmetry code $^3/_4 - y$, $^1/_4 + x$, $^1/_4 + z$. [b] Symmetry code $1 - x$, $1 - y$, $-z$. [c] Symmetry code $-^1/_4 + y$, $^5/_4 - x$, $^1/_4 - z$. [d] Cg = phenyl ring centroid.

shown in Figure 3b and Figure S1b (Supporting Information), and the shortest intermolecular C−H···O and C−H···π contacts with distances and angles are summarized in Table 2.

The observed assembly mode of helices gives rise to a noncovalent framework structure with the voids volume of about 12% of the unit cell. Solvent-accessible areas reside in special positions on the 4-fold inversion axis $\bar{4}$ (4*a* position according to Wyckoff notation). The 4-fold rotation wraps the molecule around with the metal-bonded methyl groups pointing outward. Due to the weak host−guest interactions, the solvent molecules are disordered. It is worth noting that the crystals of **1** and **2** are isostructural, which indicates that the nature of the metal center does not affect the molecular assembly of the tetrahedral aluminum and gallium complexes derived from *N*-phenylsalicylideneimine. Interestingly, our analysis of intermolecular contacts in the related structure of (*N*-methylsalicylideneiminato)-dimethylgallium, $[Me_2Ga(saldMe)]$,[27] shows that the replacement of the *N*-phenyl with an *N*-methyl group in the bidentate salicylideneiminate ligand leads to significant changes in the molecular assembly of the tetrahedral $R_2M(O,N)$ complex (the arrangement of molecules in the crystal structure of $Me_2Ga(saldMe)$ is determined, as in compounds **1** and **2**, by the $C-H_{imino}\cdots O$ interactions and result in the formation of infinite H-bonded chains assembled by weak C−H···π(Ph) interactions into the double layers without guest molecules). However, this issue will be discussed in detail together with our comprehensive analysis of the hydrogen-bond supramolecular structures of group 13 metal Schiff base complexes based on the Cambridge Structural Database.[28]

In contrast to the four-coordinate hydrogen-bonded polymeric structures of **1** and **2**, the indium analogue **3** is dimeric with $In_2(\mu\text{-}O)_2$ bridges (Figure 4). Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with two molecules per unit cell. The crystal structure of **3** comprises individual five-coordinate dimeric molecules with no unusually short intermolecular contacts. The dimer consists of a nearly planar trans-6,6,4,6,6-fused ring system with an rms deviation of atoms from the mean plane equal to 0.075 Å.

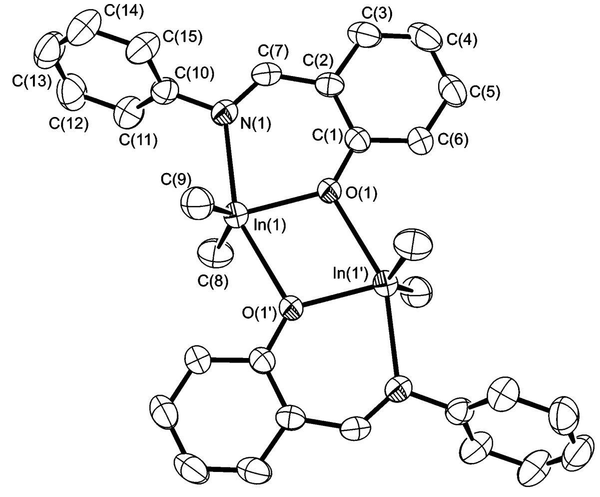

Figure 4. ORTEP diagram of $[Me_2In(saldPh)]_2$ (**3**). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

The overall molecular symmetry is crystallographically constrained to be centrosymmetric. Thus, the central $In_2(\mu\text{-}O)_2$ bridging ring is exactly planar with internal angles (O(1)−In(1)−O(1′) = 74.51(11)°) comparable to those reported for other oxygen-bridged five-coordinate dialkylindium complexes of the type $[R_2In(O,X)]_2$ (where X = O, N).[7a,29,30] The geometry at the indium atom can be described as distorted trigonal bipyramidal, with carbon atoms C(8) and C(9) and aryloxide oxygen O(1) occupying the equatorial sites. The equatorial angles range from 108.3(2) to 140.3(2)°, the latter being the angle between the methyl groups. The widening of the C−In−C angle fits well with that for other analogous five-coordinated dimeric chelate $[R_2In(O,O')]_2$ complexes, where these angles fall in the range 135−155°, and it is consistent with the trend to increase the C−M−C angle on going down group 13 (increasing s-orbital character of the M−C bonds).[7a] The In(1) atom is significantly moved (0.110(3) Å) out of the equatorial plane in the direction of the N(1) atom. The axial positions are occupied by the imino nitrogen atom N(1) and the aryloxide O(1′) atom of the second monomeric unit. The angle formed by the axial bonds, N(1)−In(1)−O(1′), is equal to 156.23(11)°, and the difference in comparison to the ideal value of 180° is caused by constraints in both the central $In_2(\mu\text{-}O)_2$ and the six-membered InOCCCN rings. The observed trigonal-bipyramidal distortion is typical for five-coordinate indium derivatives $[R_2In(O,X)]_2$ with a six-membered chelate ring, which was analyzed in our previous paper in detail.[7a] The distances In(1)−O(1) and In(1′)-O(1) (2.158(3) and 2.477(3) Å, respectively) within the central four-membered $In_2(\mu\text{-}O)_2$ ring in **3** differ significantly, despite the fact that the bridging oxygen atoms are bonded to the equivalent indium atoms. It is apparent that this results from the geometry of dimeric five-coordinated molecules, which dictates that each oxygen

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(27) Bregadze, V. I.; Furmanova, N. G.; Golubinskaya, L. M.; Kompan, O. Y.; Struchkov, Y. T.; Bren, V. A.; Bren, Z. V.; Lyubarskaya, A. E.; Minkin, V. I.; Sitkina, L. M. *J. Organomet. Chem.* **1980**, *192*, 1−15.

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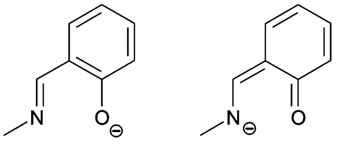
(30) Wu, X. S.; Pan, Y.; Sun, X. Z.; Zhu, Y. *Chin. J. Struct. Chem.* **1999**, *18*, 418.

atom is in the equatorial position of one indium atom and in the axial position with respect to the second atom. The six-membered metallacycle is almost planar, the maximum deviation from planarity being 0.062(2) Å for the N(1) atom. There are no notable intermolecular contacts in the structure of **3**, and the packing is controlled by the vdW interactions.

It is worth noting that generally the group 13 metal alkyl compounds, derived from the equimolar reaction between R_3M and unsaturated bifunctional organic compounds, form four-coordinate chelate complexes in solution and they are known to dimerize in the solid state.[7a,c] Hence, the observed tendency of dialkylaluminum and dialkylgallium derivatives of bifunctional salicylideneimine to form four-coordinate $R_2M(O,N)$ chelate complexes in both the solid state and solution indicates that bidentate Schiff bases act as strongly coordinating chelate ligands. In this regard, bidentate Schiff bases resemble the aforementioned symmetrical acetylacetonate ligand as well as related β-diketonates. For example, the crystal structure of $Me_2Al(bacac)$ (where bacac = 1-benzoylacetonato ligand) consists of mononuclear tetrahedral molecules which are held together entirely by very weak secondary bonds.[31] It seems likely that the molecular structures of **1** and **2** are controlled by the π-interaction of the aryloxide oxygen lone pair with the salicylideneimine extended π system, which substantially weakens the Lewis basicity of the potentially bridging oxygen and simultaneously strengthens the basicity of the chelating C=N group. One may expect essentially an equal contribution of conventional resonance structures **III** and **IV** in the monomeric chelate $R_2M(O,N)$ complexes. On the other hand, the observed dimeric structure for the analogous indium derivative **3** is fully consistent with our earlier reported conclusion concerning the Lewis acidity of the group 13 metal centers in the four-coordinate complexes.[7a] However, the analysis of the bond length alteration for **3** shows that the population of both resonance forms in this dimeric complex is similar to those observed for monomeric complexes **1** and **2**.



III **IV**

The monoalkylaluminum compound **4** crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell. The molecular structure of **4** is shown in Figure 5, and selected bond lengths and angles are given in Table 1. The geometry at aluminum is best described as trigonal bipyramidal, with the aryloxy oxygen atoms O(1) and O(2) and carbon atom C(8) occupying the equatorial plane. The angles between bonds in this plane are close to 120°, ranging between 118.49(6) and 121.72(7)°. The coordination of the chelate ligands to the aluminum center results in the formation of two six-membered rings displaying a sofa conformation. Thus, the aluminum atom is perched at 0.346(2) and 0.451(2) Å above the O(1)N(1) and O(2)N(2) chelate planes, respectively. The imino nitrogen atoms of the chelating ligands are located in axial positions, and the angle formed by the axial bonds is equal to 169.20(5)°. The central $CAlO_2N_2$ core exhibits an approximate C_2 symmetry. Nevertheless, the remaining part of the complex shows considerable deviation from this symmetry. The equatorial Al−O bond lengths (Al(1)−O(1) = 1.773(1) Å and Al(1)−O(2) = 1.777(1) Å) are quite short and comparable to those observed in the four-coordinate complex **1** or reported for simple five-coordinate complexes of the type $RAl(O,O)_2$, e.g. $MeAl(mesal)_2$ (Al−O = 1.773(2) Å).[22] They are also shorter than the Al−O bonds in monoalkylaluminum Salen derivatives, which cover the distance range from 1.78 to 1.83 Å.[28] Consequently, the axial Al−N distances (Al(1)−N(1) = 2.1034(12) Å, Al(1)−N(2) = 2.1305(13) Å) are noticeably longer then those found in Salen complexes (average Al−N distance 2.035 Å; 2.013−2.068 Å).[28] In addition, monoalkylaluminum chelate complexes derived from these unsymmetrical compounds are, like complex **4**, relatively stable, in contrast to the analogous acetylacetone derivative.[20] Thus, in this case, the bidentate Schiff base resembles unsymmetrical unsaturated β-hydroxy carbonyl compounds such as methyl salicylate and 2-aminoacethophenone. All the above observations lead to the conclusion that salicylideneimines are electronically very flexible ligand systems.

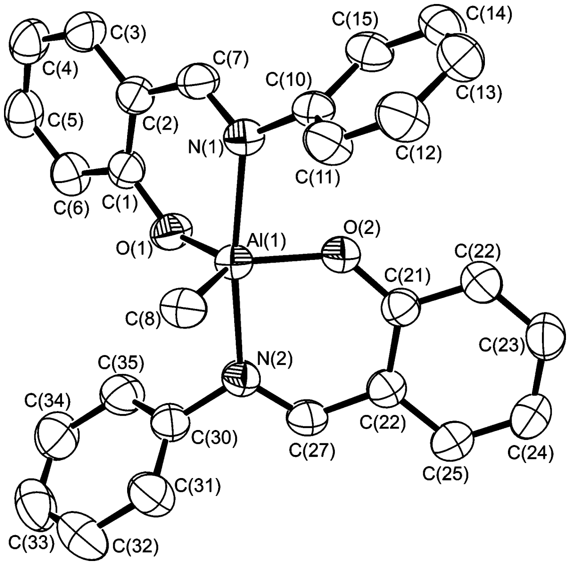


Figure 5. ORTEP diagram of $MeAl(saldPh)_2$ (**4**). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

The analysis of short intra- and intermolecular contacts in **4** does reveal $C-H_{aryl}\cdots O$ hydrogen-bonding interactions between two adjacent molecules related by the center of symmetry (Table 2, Figure 6). These interactions organize molecules into H-bonded dimers in the solid state. As may be seen from Figure 6, the phenyl group bonded to the N(1) nitrogen atom is oriented in such a way that a weak $C-H_{aryl}\cdots O$ hydrogen bonds are formed with both aryloxy oxygen atoms of the neighboring molecule, related by a center of symmetry. Furthermore, the O(1) oxygen atom is additionally engaged in the intramolecular $C-H_{aryl}\cdots O$ interactions. The salicylideneimine aromatic ring π stacking ($\pi-\pi$ distance of ~3.41 Å) is an additional motif

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[31] Lewiński, J.; Lipkowski, J.; Justyniak, I. To be submitted for publication.

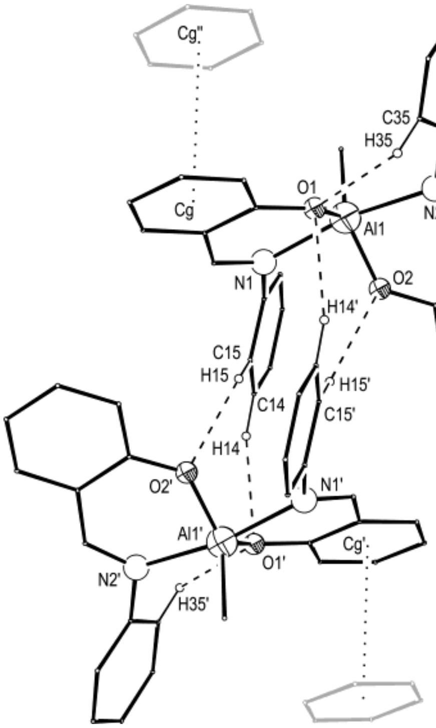

Figure 6. Hydrogen-bonded dimer of MeAl(saldPh)$_2$ (**4**) in the solid state. The dashed lines represent intra- and intermolecular C−H···O hydrogen bonds. The atoms labeled with a prime (′) are at symmetry-equivalent positions ($1 - x$, $1 - y$, $-z$). Hydrogen atoms are omitted, excluding those involved in H-bond formation.

controlling the intermolecular arrangement, as is also pointed out by dotted lines in Figure 6.

Conclusion

This report deals with the molecular and crystal structures of group 13 complexes supported by *N*-phenylsalicylideneimine. The results presented here show that bidentate Schiff bases act as strongly coordinating chelate ligands, and in this regard, they resemble the symmetrical acetylacetonato ligand as well as related β-diketonates. On the other hand, Schiff base ligands are electronically more flexible ligand systems than the latter ligands. Interestingly, the monomeric dialkylaluminum chelate complexes R$_2$Al(saldPh) are more prone to ligand redistribution reactions than the gallium and indium analogues. The X-ray crystal structure analysis indicates the C−H$_{\text{imino}}$···O, C−H$_{\text{aryl}}$···O, and C−H···π hydrogen bonds and π−π stacking as major intermolecular forces determining supramolecular structures of the studied complexes.

Experimental Section

All operations were carried out under dry nitrogen using standard Schlenk techniques. Solvents and reagents were purified and dried by standard techniques. NMR spectra were recorded on a Varian Mercury (400 MHz) spectrometer in C_6D_6 solutions. The IR spectra were recorded on a Specord M80 spectrophotometer. Molecular weight determinations were carried out cryoscopically in benzene solution. Elemental analyses and molecular weight measurements were preceded by the crystals crumbling and being maintained under high vacuum for 3 h.

Me$_2$Al(saldPh) (1). A solution of *N*-(2-hydroxybenzylidene)aniline (0.51 g, 2.61 mmol) in toluene (5 mL) was cooled to −78 °C, and Me$_3$Al (0.25 cm^3, 2.61 mmol) was added dropwise. After the addition was completed, the reaction mixture was warmed to room temperature and stirred for 0.5 h; then the volatiles were removed in vacuo. Complex **1** was obtained as yellow crystals after a recrystallization from hexane/CH$_2$Cl$_2$ solution at 0 °C. Cryoscopic molecular weight (benzene solution): formula weight calcd for $C_{15}H_{16}AlNO$ 253.28, found 253. Anal. Calcd for $C_{15}H_{16}AlNO$: C, 71.13; H, 6.37; N, 5.53. Found: C, 71.32; H, 6.57; N, 5.42. ^{1}H NMR (C_6D_6): δ −0.24 (s, 6H, Al−C*H*$_3$), 6.49−7.12 (m, 9H, Ar *H*), 7.39 (s, 1H, C*H*=N). ^{27}Al NMR (C_6D_6): δ 144. IR (cm^{-1}): 456 (m), 496 (w), 516 (m), 548 (m), 572 (m), 596 (w), 644 (m), 676 (s), 744 (m), 808 (s), 908 (s), 936 (s), 992 (m), 1004 (w), 1032 (m), 1080 (w), 1096 (w), 1128 (s), 1152 (s), 1188 (s), 1228 (m), 1248 (w), 1320 (s), 1344 (m), 1384 (s), 1420 (w), 1452 (s), 1472 (s), 1492 (s), 1528 (s), 1548 (s), 1592 (s), 1616 (s), 1696 (w), 1800 (w).

Me$_2$Ga(saldPh) (2). The reaction was carried out by using the same procedure as described for **1,** using *N*-(2-hydroxybenzylidene)aniline (0.49 g, 2.51 mmol) and Me$_3$Ga (0.25 cm^3, 2.51 mmol). Cryoscopic molecular weight (benzene solution): formula weight calcd for $C_{15}H_{16}GaNO$ 296.02, found 352 (299 after 4 h). Anal. Calcd for $C_{15}H_{16}GaNO$: C, 60.86; H, 5.45; N, 4.73. Found: C, 61.08; H, 5.63; N, 4.60. ^{1}H NMR (C_6D_6): δ 0.08 (s, 6H, Al−C*H*$_3$), 6.46−7.13 (m, 9H, Ar *H*), 7.59 (s, 1H, C*H*=N). IR (cm^{-1}) 448 (w), 504 (w), 512 (w), 544 (m), 588 (m), 612 (w), 656 (w), 796 (m), 860 (m), 892 (w 936 (w), 988 (w), 1004 (w), 1032 (w), 1080 (w), 1100 (w), 1128 (m), 1152 (s), 1184 (s), 1204 (w), 1224 (w), 1320 (m), 1348 (w), 1388 (m), 1448 (s), 1468 (s), 1488 (m), 1540 (s 1592 (s), 1616 (s).

Me$_2$In(saldPh) (3). The preparation was carried the same as described for **1,** using *N*-(2-hydroxybenzylidene)aniline (0.49 g, 2.50 mmol) and Me$_3$In (0.40 g 2.50 mmol). Cryoscopic molecular weight (benzene solution): formula weight calcd for $C_{15}H_{16}InNO$ 341.11, found 675. Anal. Calcd for $C_{15}H_{16}InNO$: C, 52.82; H, 4.73; N, 4.11. Found: C, 52.74; H, 4.79; N, 4.06. ^{1}H NMR (C_6D_6): δ 0.27 (s, 6H, Al−C*H*$_3$), 6.53−7.26 (m, 9H, Ar *H*), 7.59 (s, 1H, C*H*=N). IR (cm^{-1}) 444 (w), 488 (w), 532 (m), 576 (w), 596 (w), 848 (w), 856 (w), 896 (s), 928 (w), 988 (w), 1000 (w), 1028 (w), 1048 (w), 1080 (w), 1096 (w), 1128 (w), 1148 (m), 1172 (m), 1252 (s), 1276 (s), 1320 (m), 1348 (w), 1396 (m), 1420 (s), 1440 (s), 1464 (m), 1488 (m), 1536 (s), 1548 (m), 1592 (s), 1612 (s), 1700 (w).

MeAl(saldPh)$_2$ (4). To a solution of **1** (0,43 g, 1.00 mmol) in *n*-hexane (4 mL) was added 4-methylpyridine (0.097 g, 1.04 mmol) at room temperature. After the mixture was stirred for 5 min, the solvent and excess of 4-methylpyridine were removed in vacuo. Complex **4** was obtained as yellow crystals after recrystallization from *n*-hexane/CH$_2$Cl$_2$ solution at 0 °C. Anal. Calcd for $C_{27}H_{23}AlN_2O_2$: C, 74.64; H, 5.34; N, 6.45. Found: C, 74.56; H, 5.40; N, 6.42. ^{1}H NMR (C_6D_6): δ −0.25 (s, 3H, Al−C*H*$_3$), 6.5−7.2 (m, 18H, Ar *H*), 7.40 (s, 2H, C*H*=N). ^{27}Al NMR (C_6D_6): δ 57.

Crystallographic Studies. Single crystals of **1**−**4** suitable for X-ray diffraction studies were placed in thin-walled capillary tubes (Lindemann glass) under an inert atmosphere, which were then plugged with grease and flame-sealed. X-ray diffraction data for compounds **1**·$^1/_4C_6H_{14}$ and **4** were collected at room temperature on a Siemens P3 diffractometer and for compounds **2**·$^1/_4C_6H_{14}$ and **3** on a Kuma KM4 diffractometer equipped with a CCD detector. Crystal data and data collection and refinement parameters for all compounds are given in Table 3. The data sets were corrected for Lorentz−polarization effects. A numerical absorption correction based on a well-defined crystal shape was performed for compound **3**. In the case of **2**·$^1/_4C_6H_{14}$, an empirical correction based on multiple scanned reflections was applied using the method published by Blessing[32] and implemented in the Platon package.[33] The

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[32] Blessing, B. *Acta Crystallogr., Sect. A* **1995**, *51*, 33−38.

Table 3. Crystal Data, Data Collection, Structure Solution, and Refinement Parameters for Compounds 1−4

	$\mathbf{1}\cdot{}^{1}/_{4}C_6H_{14}$	$\mathbf{2}\cdot{}^{1}/_{4}C_6H_{14}$	**3**	**4**
formula	$C_{15}H_{16}AlNO\cdot{}^{1}/_{4}C_6H_{14}$	$C_{15}H_{16}GaNO\cdot{}^{1}/_{4}C_6H_{14}$	$C_{30}H_{32}In_2N_2O_2$	$C_{27}H_{23}AlN_2O_2$
fw	274.81	317.55	682.22	434.45
cryst size, mm	0.34 × 0.16 × 0.16	0.30 × 0.20 × 0.20	0.45 × 0.35 × 0.22	0.42 × 0.32 × 0.20
cryst syst	tetragonal	tetragonal	monoclinic	triclinic
space group, No.	$I4_1/a$, 88	$I4_1/a$, 88	$P2_1/n$, 14	$P\bar{1}$, 2
temp, K	293(2)	293(2)	293(2)	293(2)
a, Å	17.8274(17)	17.8866(19)	9.0500(12)	9.7947(14)
b, Å	17.8274(17)	17.8866(19)	9.2007(12)	10.6809(18)
c, Å	19.995(3)	20.0042(13)	17.7040(18)	12.4988(19)
α, deg	90	90	90	68.886(12)
β, deg	90	90	105.303(10)	67.907(11)
γ, deg	90	90	90	79.741(12)
V, Å^3	6354.7(13)	6400.0(10)	1421.9(3)	1128.9(3)
Z	16	16	2	2
D_{calcd}, g cm^{-3}	1.149	1.318	1.593	1.278
F(000)	2344	2632	680	456
radiation used		Mo Kα (λ = 0.710 73 Å)		
μ, mm^{-1}	0.122	1.714	1.650	0.117
θ range, deg	2.3−25.0	3.3−22.5	3.3−25.0	2.0−25.0
no. of rflns collected	4585	41 204	21 982	4256
no. of unique data, R_{int}	2807, 0.0344	2086, 0.1180	2491, 0.0585	4000, 0.0105
no. of obsd data ($I > 2\sigma(I)$)	1371	1853	2217	3405
no. of data/params/restraints	2807/235/54	2086/225/54	2491/168/0	4000/382/0
R1, wR2^a	0.0474, 0.0909	0.0566, 0.0888	0.0363, 0.0695	0.0317, 0.0856
weights *a*, *b*^{b}	0.0505, 0	0.0321, 4.20	0.0127, 3.593	0.0487, 0.174
largest resids, e Å^{-3}	+0.13, −0.15	+0.26, −0.20	+1.45, −0.57	+0.20, −0.18

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$. ^{b} $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

structures were solved by direct methods using the Shelxs-86 program.[34] Full-matrix least-squares refinement against F^2 values was carried out by using Shelxl-97.[35] All non-hydrogen atoms, except for the disordered solvent molecule in $\mathbf{2}\cdot{}^{1}/_{4}C_6H_{14}$, were refined with anisotropic displacement parameters. The hydrogen atoms in the structure of compound **4** were located from difference maps, and their positional and isotropic thermal parameters were refined. For the remaining structures the hydrogen atoms were introduced at geometrically idealized coordinates and allowed to ride on their parent C atoms. Moreover, methyl hydrogen atoms in **1**−**3** were refined as disordered groups with two positions rotated by 60° about the M−C bond. The crystal solvents in $\mathbf{1}\cdot{}^{1}/_{4}C_6H_{14}$ and $\mathbf{2}\cdot{}^{1}/_{4}C_6H_{14}$ surrounded the special positions (4*a*) with $\bar{4}$ site symmetry and were refined disordered with the sof fixed at $^{1}/_{4}$. To assist in the refinement process, all C−C bonds in disordered molecules of *n*-hexane were restrained to be equal, and thermal parameters on adjacent atoms were restrained to be similar. In all cases, the final Fourier difference maps have no significant chemical meaning. ORTEP drawings were made using Ortep3 for Windows.[36]

Acknowledgment. This work was supported by the State Committee for Scientific Research, Grant Nos. 3 T09A 066 19 and PBZ-KBN 15/T09/99/03. We are indebted to Prof. K. Woźniak from the Crystallographic Unit of the Chemistry Department (University of Warsaw) for the X-ray measurements.

Supporting Information Available: Complete tables of atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms, hydrogen positional and isotropic displacement parameters, and interatomic distances and angles for **1**−**4** and a crystal packing diagram for **2** (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

OM030331V

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