

## COMPLEXES OF ORGANOALUMINIUM COMPOUNDS WITH HEXAMETHYLPHOSPHORIC TRIAMIDE

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### SUMMARY

Hexamethylphosphoric triamide,  $(\text{Me}_2\text{N})_3\text{P}=\text{O}$ , reacts with trimethylaluminium, triethylaluminium and their mixtures to yield 1/1 complexes irrespective of the reactant mole ratio. The IR and NMR spectra indicate that the oxygen atom bonded by a donor-acceptor bond to the aluminium atom donates electrons. Between the complex and the organoaluminium compound used in excess ( $\text{P}/\text{Al} < 1/1$ ) there exists a rapid exchange of the alkyl groups attached to the aluminium. The exchange of alkyl groups also occurs between the molecules of the complex.

### INTRODUCTION

There have been numerous investigations on the complexes of organoaluminium compounds with monodentate electron donors in comparison to those with bidentate donors.

Clemens *et al.*<sup>1</sup> have studied the 1/1 complexes of ethylaluminium compounds with tetramethylhydrazine. In terms of NMR data both nitrogen atoms are equivalent and thus the aluminium atom may be bonded to either of them, thereby becoming presumably a pentacoordinate atom.

Thiele *et al.*<sup>2</sup> have obtained 2/1 complexes of trimethylaluminium with 1,2-dimethoxyethane, 1-dimethylamino-2-methoxyethane, and *N,N,N',N'*-tetramethylethylenediamine (1-dimethylamino-2-methoxyethane gives a 1/1 complex also). Among heterocyclic bidentate donors 1,4-dioxane, *N*-methylmorpholine, and *N,N'*-dimethylpiperazine yield both 2/1 and 1/1 complexes<sup>3</sup>, whereas 2,2'-bipyridine and 1,10-phenanthroline form a 1/1 complex only. In these complexes the coordination number of the aluminium atom is five<sup>3</sup>. In 1/1 complexes of organoaluminium compounds with esters, only the carbonyl oxygen coordinates with organoaluminium compound<sup>4</sup>. Diethers (*e.g.* *p*-dimethoxybenzene) form 1/1 or 1/2 complexes according to the reactant mole ratio<sup>5</sup>. *N,N'*-Butane-2,3-diylidenedianiline forms a 1/1 complex with triethylaluminium (irrespective of the reactant mole ratio) in which the aluminium atom is presumably pentacoordinate<sup>6</sup>. The 1/1 complex with dimethylcyanamide<sup>7</sup> has the structure  $\text{Me}_2\text{N}-\text{C}\equiv\text{N}\rightarrow\text{AlR}_3$ . Complexes with bidentate donors like isocyanates and isothiocyanates have been investigated by Reinheckel *et al.*<sup>8,9</sup> and others<sup>10,11</sup> but none of these could be isolated because the alkyl group is very readily

rearranged from the aluminium to the carbon atom.

The bidentate donors with a mobile hydrogen *e.g.* phosphonic acids<sup>12</sup>, aminoalcohols<sup>13</sup>, and oximes<sup>14,15</sup> have been found to react smoothly with organoaluminium compounds to yield suitable hydrocarbons and complexes involving both the donor atoms.

It is thus evident that the reaction with bidentate donors depends upon the structure of the donor molecule, basicity of individual functional groups, steric hindrance etc.

Reactions of organoaluminium compounds with polyfunctional bases have been described rather scarcely. Zambelli *et al.*<sup>16</sup> followed dismutation of methylaluminium dichloride with less than one equivalent hexamethylphosphoric triamide (HMPA) in terms of NMR spectrum. The anomalies in NMR spectrum are explained on the basis that after forming a 1/1 complex with aluminium chloride or methylaluminium dichloride, HMPA still has weakly basic functional groups capable of complexing with the aluminium atom.

McConnell *et al.*<sup>17</sup> measured the molecular weights (cryoscopically) of the complexes from the reaction of ethylaluminium dichloride and aluminium chloride with HMPA and found them to be higher than those required for 1/1 type. The high molecular weight is not surprising, since there are three nitrogen atoms in each HMPA molecule available for complexing.

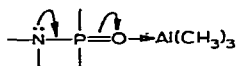
The purpose of this work is to study the reactions of organoaluminium compounds with HMPA as a polydentate donor. The primary objective is to elucidate whether the organoaluminium compound forms donor-acceptor bonds with the oxygen atom and the three nitrogen atoms simultaneously or the complexing reaction is selective and stops after the first or further stages have been attained.

## RESULTS AND DISCUSSION

Reactions of HMPA with methylaluminium and methylethylaluminium compounds and with aluminium chloride were studied in benzene or toluene at room or lower temperatures. Under these conditions only the complexing reaction proceeded. HMPA could be recovered on hydrolysis.

As the isolation of a pure organoaluminium-HMPA complex of a well-defined P/Al ratio is no proof of the non-existence of less-stable complexes of different P/Al ratios, the IR and NMR spectra and molecular weights of the complexes were run in benzene or toluene prior to their isolation.

The IR spectra of (1/1), (1.05/1), (1/2) and (2/1 by mole) HMPA/trimethylaluminium solutions in benzene are summarized in Table 1. In 1/1 complex, the P=O stretching frequency is lowered by 42 cm<sup>-1</sup> as compared to that in HMPA, indicating that trimethylaluminium forms complexes via oxygen. At the same time the two N-P frequencies increase by 11 and 15 cm<sup>-1</sup> which could be explained in terms of strengthening of the N-P bond owing to the withdrawal of electrons by the aluminium atom and the shift of the electron pair of nitrogen atom towards phosphorus.



The absence of 1212 cm<sup>-1</sup> band (free P=O group) rules out the formation of

TABLE 1  
IR SPECTRA OF THE HMPA-Me<sub>3</sub>Al COMPLEXES IN BENZENE AT ROOM TEMPERATURE<sup>a</sup>

HMPA ν(cm <sup>-1</sup> )	HMPA/Me <sub>3</sub> Al mole ratio					Assignment
	1/1		1.05/1	1/2	2/1	
	ν(cm <sup>-1</sup> )	Δν(cm <sup>-1</sup> )	ν(cm <sup>-1</sup> )	ν(cm <sup>-1</sup> )	ν(cm <sup>-1</sup> )	
2980 w	2990 w		2990 w	2990 w	2990 (sh)	CH <sub>3</sub> stretch
2880 s	2900 s		2900 s	2900 s	2900 s	
2780 w	2800 w		2800 w	2800 w	2800 m	
1480 w	1488 w		1488 w	1488 w	1488 w	
1458 m	1458 m		1458 m	1458 m	1458 m	
1295 s	1300 s		1300 s	1300 s	1298 vs	
1212 vs			1212 (sh)		1212 vs	P=O stretch
1168 m	1170 vs	-42	1170 vs	1170 vs	1170 vs	
1146 w	1146 (sh)		1146 (sh)	1146 (sh)	1146 (sh)	
1064 w	1068 m		1068 m	1068 m	1066 m	
982 vs (b)	993 vs	+11	993 vs	993 vs	982 vs 993 vs	N-P
743 vs (b)	758 m (b)	+15	743 vw 758 m (b)	758 s (b)	743 vs (b) 758 m (b)	N-P stretch

<sup>a</sup> w = weak, m = medium, s = strong, v = very, (b) = broad, (sh) = shoulder.

complexes at the ratio 1/1 via oxygen and nitrogen atoms simultaneously. In 1/2 ratio the characteristic bands of the complex only are found, whereas at 2/1, intense bands both due to the complex and free HMPA are observed.

The bands from IR spectra of the HMPA/methylaluminium compound and HMPA/aluminium chloride solutions in benzene are summarized in Table 2 and

TABLE 2  
IR SPECTRA OF THE 1/1 HMPA-Me<sub>n</sub>AlCl<sub>3-n</sub> AND HMPA-AlCl<sub>3</sub> COMPLEXES IN BENZENE AT ROOM TEMPERATURE

HMPA ν(cm <sup>-1</sup> )	Complexes of HMPA with								Assignment
	Me <sub>3</sub> Al		Me <sub>2</sub> AlCl		MeAlCl <sub>2</sub>		AlCl <sub>3</sub>		
	ν(cm <sup>-1</sup> )	Δν(cm <sup>-1</sup> )	ν(cm <sup>-1</sup> )	Δν(cm <sup>-1</sup> )	ν(cm <sup>-1</sup> )	Δν(cm <sup>-1</sup> )	ν(cm <sup>-1</sup> )	Δν(cm <sup>-1</sup> )	
1212 vs	1170 vs	-42	1180 vs		1180 vs		1180 m		P=O stretch
1168 m			1160 vs	-52	1142 vs	-70	1142 vs	-70	
1146 w	1146 (sh)		1146 (sh)				1112 m		
982 vs (b)	993 vs	+11	995 vs	+13	998 vs	+16	1000 vs	+18	N-P
743 vs (b)	758 m (b)	+15	760 vs	+17	763 vs	+20	765 vs	+22	N-P stretch

represented graphically in Fig. 1. In complexing with HMPA, the organoaluminium compounds shift the ν(P=O) band towards lower frequencies which is related to the acid strength of the organoaluminium compound and rises in the order:

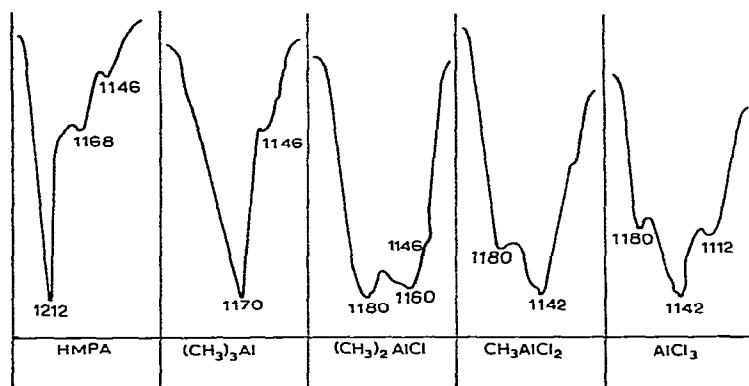
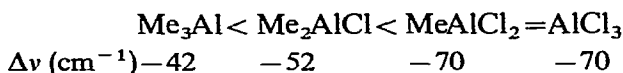


Fig. 1. The IR spectra of the HMPA/methylaluminum compound and HMPA/aluminum chloride solutions in benzene in the 1250–1100  $\text{cm}^{-1}$  region.



The small increase in N–P frequency (within the range 15–22  $\text{cm}^{-1}$ ) is due to the interaction of nitrogen atom with the aluminium atom placed far away.

The above data are consistent with those on the shifts of the  $\text{C}\equiv\text{N}$  band in nitrile complexes<sup>18</sup> and the  $\text{C}=\text{O}$  and  $\text{C}-\text{O}-\text{R}$  bands in the ester complexes<sup>19</sup>.

The other characteristic bands in addition to those discussed above are summarized in Table 2 and Fig. 1. They are presumably associated with the overlapping of the 1168 and 1146  $\text{cm}^{-1}$  bands of free HMPA with those of the complexes.

The effect of the P/Al ratio on band position in the IR spectra of the HMPA complexes with dimethylaluminium chloride and methylaluminium dichloride was found to be identical with that for trimethylaluminium.

To check these conclusions, we studied NMR spectra of the HMPA/trimethylaluminium solutions in toluene at various P/Al mole ratios (Table 3, Fig. 2).

TABLE 3

NMR SPECTRA OF HMPA/ $\text{Me}_3\text{Al}$  MIXTURES IN TOLUENE

Molar ratio HMPA/ $\text{Me}_3\text{Al}$	Temp. (°C)	Chem. shift <sup>a</sup> of $\text{CH}_3-\text{Al}$ in Hz
0/1	20	440
1/1	20	447
1/4	20	445
1/5	20	442
1/10	20	441
0/1	-68	418, 453
1/1	-70	433
1/2	-68	418, 433, 451
1/3	-68	417, 432, 451
1/4	-62	418, 432, 451
1/5	-62	416, 433, 451
1/10	-63	416, 433, 451

<sup>a</sup> All shifts are relative to the ring protons of toluene as the standard.

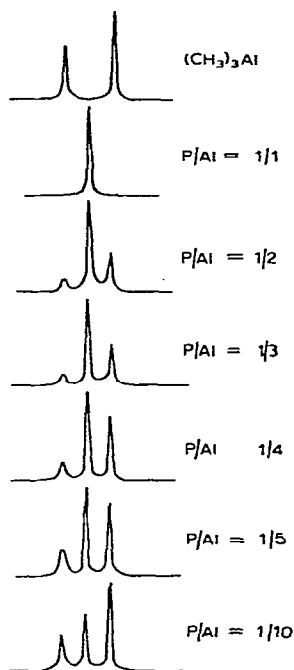
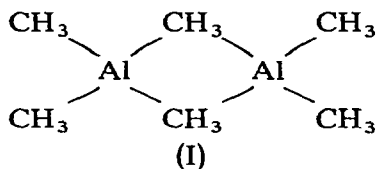


Fig. 2. The proton NMR spectra of mixtures of HMPA and trimethylaluminium in toluene at low temperature.

At room temperature in toluene trimethylaluminium shows only a single peak (at 440 Hz upfields) measured with reference to the ring protons of toluene. At  $-68^{\circ}$ , it splits into two (418 and 453 Hz), with an intensity distribution of 1/2. It could be explained in terms of rapid exchange of methyl groups in trimethylaluminium dimer (I) thereby exhibiting two peaks characteristic of bridge methyl groups (418 Hz) and terminal methyl groups (453 Hz).



In an equimolar HMPA/trimethylaluminium solution in toluene at room temperature only one peak (447 Hz) is observed. If the peak at 447 Hz corresponds to  $\text{CH}_3\text{-Al}$  methyl protons in the 1/1 complex, then the downfield shift of this peak with an excess of trimethylaluminium may be explained by considering a rapid exchange of methyl groups between the complex and free trimethylaluminium. The larger is the amount of trimethylaluminium, the closer will be the position of the mixture peak to that of pure trimethylaluminium.

At  $-70^{\circ}$ , the equimolar HMPA/trimethylaluminium solution ( $\text{P/Al}=1/1$ ) in toluene shows only a single peak (433 Hz), indicating that all trimethylaluminium is used up in the complexing reaction and either oxygen or nitrogen can donate electrons. In case trimethylaluminium should form the complex partially via oxygen

and partially via nitrogen, then the NMR spectrum would exhibit two methyl peaks due to the groups  $O \rightarrow AlMe_3$  and  $N \rightarrow AlMe_3$ .

At P/Al 1/2, in addition to the unaffected 433 Hz peak of the complex, two more peaks (418 and 451 Hz) are observed with an intensity distribution of 1/2, identical as for pure trimethylaluminium. It is an obvious proof that only the 1/1 complex is formed in toluene and the excess of trimethylaluminium remains uncomplexed. Addition of trimethylaluminium in still greater amounts (3- 4- 5- and 10-fold excess) does not change the chemical shifts. The only feature that changes is the intensity distribution of the peak due to the complex to the peaks of uncomplexed trimethylaluminium.

The NMR spectra of the HMPA-dimethylethylaluminium ( $Me_2AlEt$ ) and HMPA-methyldiethylaluminium ( $MeAlEt_2$ ) complexes (P/Al 1/1) are summarized in Table 4 and presented in Fig. 3. The spectra exhibit three sharp peaks characteristic of  $CH_3-Al$  protons in three organoaluminium compounds. The 434 Hz peak corresponds to the chemical shift of the methyl groups in the HMPA  $\cdot AlMe_3$  complex

TABLE 4

NMR SPECTRA OF MIXTURES OF HMPA,  $Me_3Al$  AND  $Et_3Al$  IN TOLUENE AT LOW TEMPERATURE

Molar ratio of reagents HMPA/ $Me_3Al$ / $Et_3Al$	Molar ratio P/Al	Chem. shift of $CH_3-Al$ (Hz)	Chem. shift of $C_2H_5-Al$ $CH_2$ signal (Hz)
3/2/1	1/1	434; 437; 440	390; 395; 400; 405
3/1/2	1/1	434; 437; 440	389; 394; 399; 404
1/1/1	1/2	416; 432; 435; 438; 450	390; 395; 400; 405
1/1/0.5	1/1.5	417; 433; 436; 439; 451	392; 397; 402; 407
1/0/1	1/1		388; 396; 402; 408

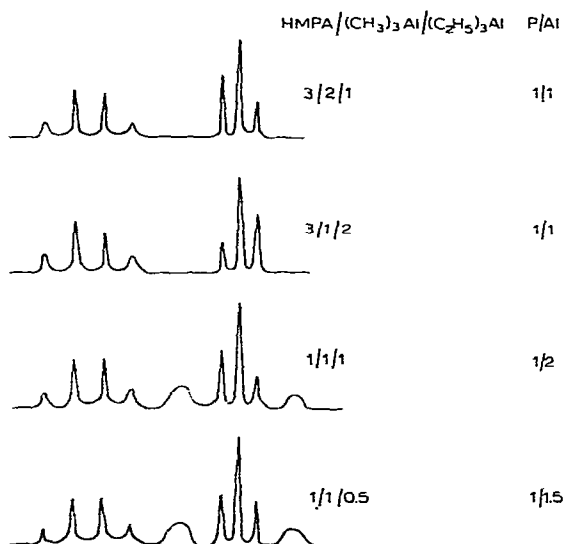
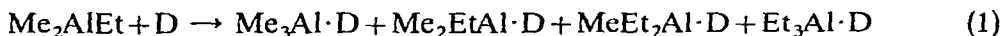


Fig. 3. The proton NMR spectra of mixtures of HMPA, trimethyl- and triethylaluminium in toluene at low temperature.

(Table 3); the 437 Hz and the 440 Hz peaks are attributed to the methyl groups in the complexes  $\text{HMPA} \cdot \text{AlMe}_2\text{Et}$  and  $\text{HMPA} \cdot \text{AlMeEt}_2$ , respectively. The formation of these complexes is explainable only in terms of the rapid exchange of aluminium-borne alkyl groups. At low temperatures ( $-60^\circ$ ) it is obstructed and the reaction mixture contains all the four complexes of HMPA with trimethylaluminium, dimethylethylaluminium, methyldiethylaluminium, and triethylaluminium, *viz.*,



(where D = donor)

The first three complexes are resolved in the NMR spectrum because of the methyl groups being attached to different moieties. Mole<sup>20-22</sup> recorded a similar resolution of the methyl peaks in complexes with ether, tetrahydrofuran, and pyridine. In dimethylethylaluminium the Me/Et ratio is twice as high as that in methyldiethylaluminium, therefore the intensity distribution of the methyl peaks varies a great deal in the corresponding complexes. In the first complex the trimethylaluminium peak is intense, whereas in the second complex the methyldiethylaluminium peak is more pronounced.

The NMR spectra of these two complexes exhibit a quartet attributable to the  $\text{CH}_2$  protons in the aluminium-borne ethyl group. The quartet produced by the HMPA-triethylaluminium complex (Table 4) occupies a similar position. In this case the positions of the ethyl peaks are unaffected by their moieties.

If an equimolar amount of triethylaluminium is added to the 1/1 HMPA-trimethylaluminium complex in toluene as solvent, alkyl exchange also takes place. Therefore, at low temperatures the NMR spectrum exhibits three sharp peaks attributable to the above-mentioned complexes of HMPA with trimethylaluminium, dimethylethylaluminium, and methyldiethylaluminium (432, 435, and 438 Hz, respectively). In addition, the spectrum reveals two broad peaks (416 and 450 Hz) positions of which correspond to the chemical shifts of free trimethylaluminium peaks (Table 3). As a result of group exchange, besides the mixture of complexes, uncomplexed alkylaluminium compounds, *viz.*,  $\text{Me}_6\text{Al}_2$ ,  $\text{Me}_5\text{Al}_2\text{Et}$ ,  $\text{Me}_4\text{Al}_2\text{Et}_2$ ,  $\text{Me}_3\text{Al}_2\text{Et}_3$ ,  $\text{Me}_2\text{Al}_2\text{Et}_4$ ,  $\text{MeAl}_2\text{Et}_5$ , and  $\text{Al}_2\text{Et}_6$ , with the bridging and the terminal methyl groups are also found. The chemical shifts of these groups are presumably only slightly different from the positions of the bridging and the terminal methyl peaks in trimethylaluminium. These broad peaks can therefore be explained in terms of the presence of a number of dimers with methyl groups in various positions.

An inverse addition of the reactants, *i.e.* of the 1/1 HMPA-triethylaluminium complex to an equimolar amount of trimethylaluminium does not change the pattern. But the modification of the Me/Et ratio reflects itself in the varied intensity distribution of the peaks attributable to the HMPA-trimethylaluminium and HMPA-methyldiethylaluminium complexes.

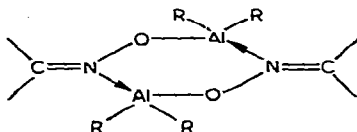
The complexes were isolated to check whether or not the composition is subject to change when pure. Elemental analyses and the molecular weights are listed in Table 5.

The studies disclosed that of the four potential donor atoms in the HMPA molecule, the oxygen atom is the only actual donor. The most important reasons for it are (i) the decrease in the donating power of the nitrogen atoms on account of the withdrawal of electrons by the complexed aluminium (II) and (ii) a considerable steric





The complexes obtained with the donors having a mobile hydrogen, *e.g.* phosphonic acids<sup>12</sup>, aminoalcohols<sup>13</sup>, and oximes<sup>14</sup> may be treated as internal complexes, because formally the aluminium atom is bonded simultaneously to both donors by the covalent and donor-acceptor bonds.

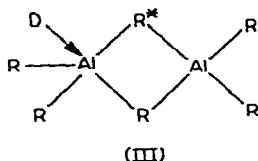


The alkyl group exchange between the complex and a free organoaluminium compound can be represented as:



where  $D = \text{HMPA}$ ;  $R = \text{CH}_3$  or  $\text{C}_2\text{H}_5$ ; and  $R^*$  is the group exchanged.

According to Mole *et al.*<sup>16</sup>, the mechanism of the exchange reaction (2) may be represented in terms of structure (III).



It represents a transition state with one pentacoordinated aluminium atom and the other tetracoordinate. With the HMPA complex, the structure (III) is unlikely because of considerable steric hindrance. Also, dissociation of the complex  $D \cdot AlR_3$  to  $D + AlR_3$  followed by a rapid exchange between the free molecules of organoaluminium compound should be ruled out, because HMPA is a strong Lewis base and at room temperature the complex is very unlikely to dissociate.

The authors believe that the plausible mechanism of the reaction (2) involves following steps:

(i). Abstraction of an anion  $R^-$  from the aluminium atom in the complex:



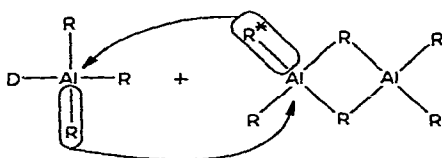
(ii). Reaction of this anion with the organoaluminium dimer:



(iii). Reconstitution of the complex molecule with the exchanged alkyl group:



The anion  $R^-$  is abstracted from the complex presumably by the action of the approaching dimer molecule and in further stages the reaction proceeds according to:



The strong base makes abstraction of the anion  $R^-$  easier and at the same time stabilizes the resulting cation  $D \cdot \dot{A}lR_2$ .

Similar interpretation may be applied to the mechanism of the exchange of alkyl groups between HMPA-complexed organoaluminium compound molecules. The difference is that the anion  $R^-$  attacks the aluminium atom in the complex  $D \cdot AlR_3$  and not in the dimer  $R_6Al_2$ . This presumably is the rate-determining step because in the complex the electron-accepting properties of aluminium are considerably reduced.

## EXPERIMENTAL

### 1. Reactants

Trimethylaluminium, triethylaluminium, and mixed alkylaluminium compounds were prepared by conventional methods.

Hexamethylphosphoric triamide (Fluka's pure grade) was used without any further purification.

Commercially pure hydrocarbons were redistilled from sodium in a nitrogen atmosphere and stored over molecular sieves (type 4A).

### 2. Method

All operations were carried out in an atmosphere of dry deoxygenated nitrogen. Trimethylaluminium was added to a solution of hexamethylphosphoric triamide in required amounts. The solution thus obtained was used for further investigations. The reaction mixtures were cooled to  $-60^\circ$  to isolate the complexes. The white crystalline sediment was washed twice with n-heptane or petroleum ether and then dried *in vacuo* at room temperature.

### 3. Molecular weights

The molecular weights were measured cryoscopically in benzene with a standard freezing point depression apparatus modified so as to carry out the measurements in an atmosphere of nitrogen.

### 4. Spectra

Temperature-dependent NMR spectra were recorded on a JEOL JNM-C-60H spectrometer. The spectra were run in toluene (at room temperature and at  $-60^\circ$ ) and toluene ring protons being used as internal standard.

A Perkin-Elmer spectrophotometer was used to record IR spectra. Solution spectra were run in benzene and toluene at room temperature.

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