

Synthesis of S-Methylisopropylidenehydrazinecarbodithioate Complexes of Aluminum

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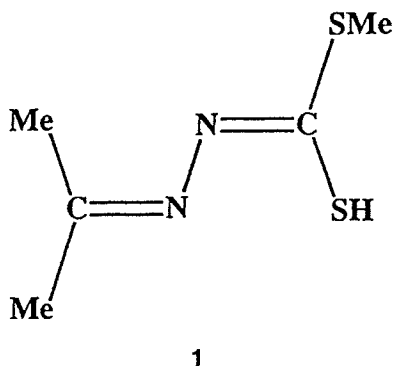
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ABSTRACT

Aluminum(III) complexes of S-methylisopropylidenehydrazinecarbodithioate have been synthesized and characterized by ^1H , ^{13}C and ^{27}Al NMR.

Transition metal complexes of the monoanionic Schiff base ligand S-methylisopropylidenehydrazinecarbodithioate (HNS) (1) have been shown to be stoichiometric transmetalating agents for the replacement of copper in a variety of tetranuclear complexes [1]. The driving force in these systems is the formation of the insoluble $[\text{Cu}(\text{NS})_x]$ or highly stable $\text{Cu}(\text{NS})_2$ coproducts.

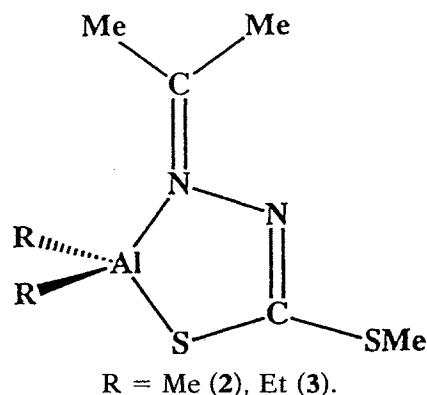


The desire to extend this transmetalation reaction to main group metals prompted an investi-

gation of the NS complexes of aluminum (III). The results of these studies are reported herein.

RESULTS AND DISCUSSION

The reaction of AlR_3 (Me, Et) with HNS leads to $\text{AlR}_2(\text{NS})$ [R = Me (2), Et (3)] in addition to the evolution of the appropriate alkane.



Compounds 2 and 3 have been fully characterized by elemental analysis and NMR spectral data (Table 1). The ^1H and ^{13}C NMR data for 2 and 3 are consistent with the proposed formula. The ^{27}Al NMR spectra indicate that the aluminum is four-coordinate tetrahedral [2], suggesting a bidentate chelating coordination of the NS ligand, as has been previously observed for its transition metal complexes [3].

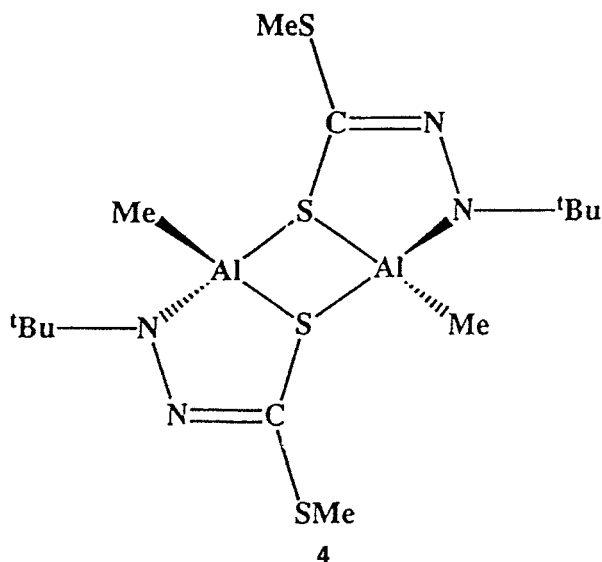
Compound 2 readily decomposes on heating above ambient temperature in toluene, resulting in alkylation of the NS ligand and the formation of $\text{AlMe}(\text{NS}^*)$ (4).

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TABLE 1 ^1H , ^{13}C and ^{27}Al NMR data for new aluminum compounds^a

Compound	^1H	Assignment	^{13}C	Assignment	^{27}Al	W_1
(2) $\text{AlMe}_2(\text{NS})$	2.08 (s)	3H	SCH_3	179.59	$\text{N}=\text{CS}_2$	168 3,910
	1.51 (s)	3H	$\text{C}(\text{CH}_3)_2$	174.53	$\text{N}=\text{CMe}_2$	
	1.45 (s)	3H		24.12	$\text{C}(\text{CH}_3)_2$	
	-0.27 (s)	6H	$\text{Al}-\text{CH}_3$	21.40	SCH_3	
				15.90	$\text{Al}-\text{CH}_3$	
				-7.31		
(3) $\text{AlEt}_2(\text{NS})$	2.14 (s)	3H	SCH_3	179.31	$\text{N}=\text{CS}_2$	174 3,880
	1.77 (s)	3H	$\text{C}(\text{CH}_3)_2$	174.52	$\text{N}=\text{CMe}_2$	
	1.74 (s)	3H		24.34	$\text{C}(\text{CH}_3)_2$	
	1.14 (t)	6H	$\text{Al}-\text{CH}_2\text{CH}_3$	21.45	SCH_3	
	$J(\text{H}-\text{H}) = 7.6$			15.92	$\text{Al}-\text{CH}_2\text{CH}_3$	
	0.18 (q)	4H	$\text{Al}-\text{CH}_2$	9.45	$\text{Al}-\text{CH}_2$	
	$J(\text{H}-\text{H}) = 7.6$			1.52		
(4) $[\text{AlMe}(\text{NS}^*)]_2$	2.11 (s)	3H	SCH_3	171.32	$\text{N}=\text{CS}_2$	164 1,970
	1.17 (s)	9H	$\text{C}(\text{CH}_3)_3$	60.01	$\text{C}(\text{CH}_3)_3$	
	-0.08 (s)	3H	$\text{Al}-\text{CH}_3$	28.93	$\text{C}(\text{CH}_3)_3$	
				16.11	SCH_3	
				-7.23	$\text{Al}-\text{CH}_3$	
(6) $\text{Al}(\text{NS})_3$	2.47 (s)	3H	SCH_3	200.66	$\text{N}=\text{CS}_2$	10 120
	1.45 (s)	3H	$\text{C}(\text{CH}_3)_2$	151.13	$\text{N}=\text{CMe}_2$	
	0.58 (s)	3H		24.46	CCH_3	
				17.68	SCH_3	
				14.86	CCH_3	

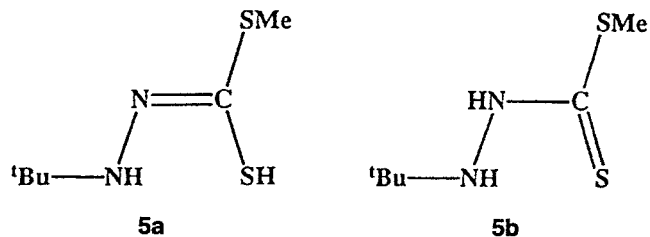
^aIn ppm relative to SiMe_4 (^1H and ^{13}C) and external $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (^{27}Al); J and W_1 values in Hz.



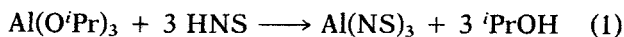
As with **2** and **3**, the ^{27}Al NMR spectrum of **4** (Table 1) is consistent with a tetrahedral four-coordinate geometry around the aluminum [2], suggesting that **4** exists as a symmetrically bridged dimer in solution. Steric requirements would dictate that the sulfur would act as the bridging ligand in preference to nitrogen. We have, however, been unable to obtain suitable crystals for X-ray diffraction to confirm this hypothesis.

Although the facile alkylation of organic nitriles and imines has been reported for a variety of alkyl and aryl groups [4], we observed no alkyl transfer for compound **3** even at elevated temperatures.

The hydrolysis of **4** yields *S*-methyl-*tert*-butylhydrazine carbodithioate (H_2NS^*) (**5**), which has been characterized by ^1H and ^{13}C NMR (see Experimental). As with HNS [5], the presence of a broad downfield peak in the ^1H NMR suggests that **5** exists as **5a** (and not **5b**) in solution.

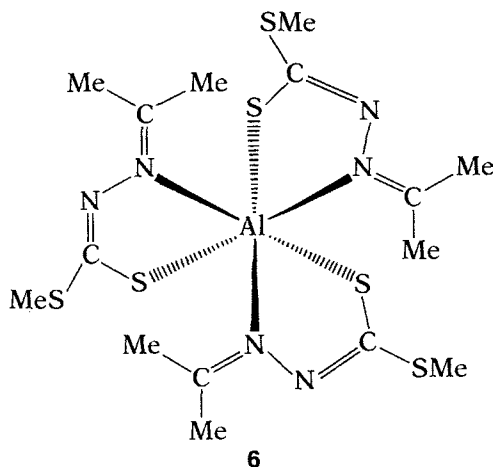


The compound $\text{Al}(\text{NS})_3$ (**6**) was first obtained in moderate yield from the reaction of AlEt_3 with HNS. An improved procedure, however, is the reaction of HNS with $\text{Al}(\text{O}^i\text{Pr})_3$ (Equation 1). Unlike the alkyl derivatives (**2**–**4**), **6** is only sparingly soluble in common organic solvents.



The ^{27}Al NMR for **6** (Table 1) is consistent with

a six-coordinate octahedral coordination geometry around aluminum [2]. The presence of one set of peaks for the ligand methyls in the ^1H and ^{13}C NMR suggests that **6** is either fluxional or exists as the *fac*-isomer. The large upfield shift of the protons of the methyl *cis* to the Al (see Table 1) is, however, likely due to a rigid geometry in which the methyl group is held within the shielding region of the $\text{C}=\text{N}-\text{N}=\text{C}$ π -system of an orthogonal ligand.



The application of compounds **2**, **3**, and **6** as transmetalating agents for the replacement of copper in tetranuclear halide clusters is being investigated, and these studies will be presented elsewhere.

EXPERIMENTAL

All manipulations were carried out under dinitrogen. Solvents were distilled and degassed before use. Melting points were determined in sealed capillaries and are uncorrected. NMR spectra were recorded in C_6D_6 on Bruker AM-400 (^1H and ^{13}C) and WM-300 (^{27}Al) spectrometers [δ in ppm relative to SiMe_4 (^1H and ^{13}C) and external $\text{Al}(\text{H}_2\text{O})_6^{3+}$ (^{27}Al)]. *S*-methylisopropylidenehydrazinecarbodithioic acid, HNS, was prepared according to published procedures [4]. Satisfactory elemental analysis was obtained for all new compounds.

$\text{AlMe}_2(\text{NS})$ (**2**)

To a hexane (30 mL) solution of HNS (0.23 g, 1.40 mmol) at room temperature was added AlMe_3 (0.70 mL, 2M solution in hexane, 1.40 mmol). Gas was evolved immediately following addition and the solution became yellow/orange. After stirring for 1 h, the solvent was removed under vacuum and the residue recrystallized from Et_2O (20 mL) at -20°C to give a yellow-orange solid. Yield: 0.24 g, 78%, mp $80-81^\circ\text{C}$ (dec).

$\text{AlEt}_2(\text{NS})$ (**3**)

To a solution of HNS (0.36 g, 2.19 mmol) in toluene (30 mL) at room temperature was added AlEt_3 (2.2 mL, 1M solution in hexane, 2.20 mmol). The solution immediately turned orange. After stirring for 2 h, the solvent was removed under vacuum to give an orange oil that was tritiated with pentane (10 mL). The resulting orange solid was isolated by filtration and dried under vacuum. Yield: 0.38 g, 69%, mp $108-110^\circ\text{C}$ (dec).

$[\text{AlMe}(\text{NS}^*)]_2$ (**4**)

Method 1. To a toluene (35 mL) solution of HNS (0.46 g, 2.80 mmol) was added AlMe_3 (1.4 mL, 2M solution in hexane, 2.80 mmol). Warming in a hot water bath for 2 h gave a bright orange solution. Removal of the solvent under vacuum and recrystallization from hexane/ Et_2O (1:1 mixture, -20°C) gave orange crystals. Yield: 0.58 g, 94%, mp 130°C (dec).

Method 2. A toluene (50 mL) solution of $\text{AlMe}_2(\text{NS})$ (0.48 g, 2.18 mmol) was refluxed for $\frac{1}{2}$ h to give a bright orange solution. Removal of the solvent under vacuum gave an orange powder. Yield: 0.47 g, 98%.

H_2NS^* (**5**)

To an Et_2O (25 mL) solution of $\text{AlMe}(\text{NS}^*)$ (0.50 g, 2.27 mmol) was added H_2O (10 mL). After vigorous gas evolution ceased, the Et_2O layer was separated and dried over MgSO_4 . Filtration and removal of the solvent gave a low melting white solid. Yield: 0.36 g, 88%.

NMR. ^1H : 8.26 (1H, s, SH), 3.33 (1H, s, NH), 2.42 (3H, s, SCH_3), 0.98 [9H, s, $\text{C}(\text{CH}_3)_3$]. ^{13}C : 158.21 ($\text{N}=\text{CS}_2$), 27.43 [$\text{C}(\text{CH}_3)_3$], 26.97 [$\text{C}(\text{CH}_3)_3$], 18.11 (SCH_3).

$\text{Al}(\text{NS})_3$ (**6**)

Method 1. To a toluene (50 mL) solution of HNS (0.50 g, 3.05 mmol) was added AlEt_3 (1.0 mL, 1.00 mmol). The solution was refluxed for 5 h, after which the resulting orange suspension was filtered and dried under vacuum. Yield: 0.31 g, 60%, mp 265°C (dec).

Method 2. Toluene (60 mL) was added to HNS (0.5 g, 3.05 mmol) and $\text{Al}(\text{O}^i\text{Pr})_3$ (0.20 g, 0.98 mmol) in a Schlenk fitted with a 5' vigreux column. The reaction mixture was refluxed until 20 mL of toluene/ $^i\text{PrOH}$ had been removed. The resulting orange suspension was filtered and dried under vacuum. Yield: 0.48 g, 95%.

ACKNOWLEDGMENT

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