Organometallics 1984, *3*, 271-274

Reaction of K_2SO_4 with $AlMe_3$ and the Crystal Structures of $K_2[Al_4Me_{12}SO_4]$ and $K_2[Al_4Me_{12}SO_4]\cdot 0.5$*p*-xylene

Robin D. Rogers and Jerry L. Atwood*

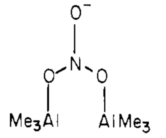
Department of Chemistry, University of Alabama, University, Alabama 35486

Received July 28, 1983

Trimethylaluminum reacts with stoichiometric quantities of potassium sulfate in aromatic solvents to form a liquid clathrate of composition $K_2[Al_4Me_{12}SO_4]\cdot n$ aromatic. With toluene the air-sensitive $K_2[Al_4Me_{12}SO_4]$, I, resulted, while for *p*-xylene the complex was found to have the composition $K_2[Al_4Me_{12}SO_4]\cdot 0.5$*p*-xylene, II. I crystallizes in the monoclinic space group $P2_1/c$ with lattice parameters $a = 10.223$ (4) Å, $b = 20.225$ (7) Å, $c = 14.039$ (4) Å, $\beta = 112.20$ (3)°, and $D_{calcd} = 1.14$ g cm^{-3} for $Z = 4$. II also crystallizes in $P2_1/c$ with $a = 9.773$ (3) Å, $b = 15.497$ (6) Å, $c = 20.442$ (9) Å, $\beta = 92.51$ (3)°, and $D_{calcd} = 1.11$ g cm^{-3} for $Z = 4$. Least-squares refinement gave final conventional R values of 0.095 for I (1576 observed reflections) and 0.055 for II (1300 observed reflections). In both cases the four $AlMe_3$ units are bonded to separate oxygen atoms of the SO_4^{2-} group. The Al–O distances average 1.90 (2) Å for I and 1.91 (4) Å for II.

Introduction

In the course of our investigation of the reaction of aluminum alkyls with MX, many unusual chemical events have been observed. One of the most remarkable has been the thermal stability of complexes in which X is a high-oxygen content anion.[1] Thus, KNO_3 or KO_2 reacts with $AlMe_3$ to yield compounds that may be refluxed in toluene without decomposition.[2] In order to gain some understanding of the stability of these species, as well as their solution behavior in general,[3] we have carried out numerous X-ray structural investigations. In the main there are 1:1, $M[AlR_3X]$, and 1:2, $M[Al_2R_6X]$, compounds. The 1:1 substances are of less interest than the 1:2, and we have concentrated on the latter. For $K[Al_2Me_6NO_3]$ there are two possible types of anionic attachment, **1** and **2**. **1** pertains,[4] but there is precedent for **2** in $[Al_2Me_6O_2]^-$, **3**,[5] and $[Al_2Me_6OPh]^-$, **4**.[6] It is also important to note that no 1:3 nitrato complex, i.e., $[Al_3Me_9NO_3]^-$, has been encountered, although **1** rapidly exchanges $AlMe_3$ units with excess $AlMe_3$. The same situation is also found for the acetate **5**.[7] In fact, the only example of a 1:3 complex is the rather exotic $[Al_3Me_9SeMe]^-$, **6**.[8] Dehnicke has reported[9] a 1:4 complex of composition $[Al_4Me_{12}SCN]^-$, but we were unable to substantiate the claims.[10] More recently, Dehnicke characterized $[Al_4Me_{12}SO_4]^{2-}$, $[Al_4Me_{12}S_2O_3]^{2-}$, and $[Al_4Me_{12}S_2O_6]^{2-}$ by vibrational spectroscopic techniques.[11] Since this seemed to present an opportunity to verify the 1:4 stoichiometry structurally, we undertook the study of the reaction of K_2SO_4 with $AlMe_3$.



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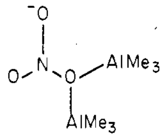

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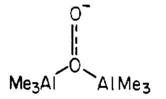

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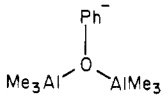

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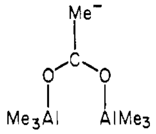

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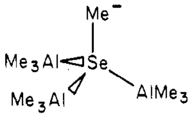

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Discussion

Regardless of the stoichiometry of the reaction of K_2SO_4 with $AlMe_3$, only the 1:4 complex has been isolated. Attempted synthesis of the 1:1, 1:2, or 1:3 moieties led in all cases to the 1:4 complex and unreacted K_2SO_4. It is interesting to note that $K_2[Al_4Me_{12}SO_4]$ forms a normal liquid clathrate, and if the 1:4 ion is the dominant species in solution, it is the first instance of this behavior for a compound of such stoichiometry.

In the course of the investigation, two crystalline materials were isolated, $K[Al_4Me_{12}SO_4]$ (I) and $K[Al_4Me_{12}SO_4]\cdot 0.5$*p*-xylene (II). The mode of attachment of the four $AlMe_3$ units to the SO_4^{2-} ion is clearly shown in Figures 1 and 2 for I and II, respectively. The major difference in the two anions involves a rotation about the O(1)–Al(1) bond and can doubtless be ascribed to packing effects. The Al–O bond lengths range from 1.88 (1) to 1.92 (1) Å and average 1.90 (2) Å for I, while the corresponding values are 1.886 (9)–1.977 (9) and 1.91 (3) Å for II (Table I). The average values correspond most closely to those of the nitrate complexes: 1.91 (3) Å in $K[Al_2Me_6NO_3]$,[4] 1.930 (6) Å in $K[AlMe_3NO_3]\cdot C_6H_6$,[4] and 1.92 (1) Å in [K·dibenzo-18-crown-6]$[AlMe_3NO_3]\cdot 0.5C_6H_6$.[12] Complexes such as $[NMe_4][Al_2Me_6MeCOO]$,[7] $[NMe_4]$-

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[1] All of the compounds with aluminum alkyls are oxygen and water sensitive.

[2] The KO_2 must be activated by the presence of a crown ether. Otherwise, an aluminoxane is formed without the isolation of a discrete superoxide complex: Atwood, J. L.; Hrncir, D. C.; Priester, R. D.; Rogers, R. D. *Organometallics* **1983**, *2*, 985.

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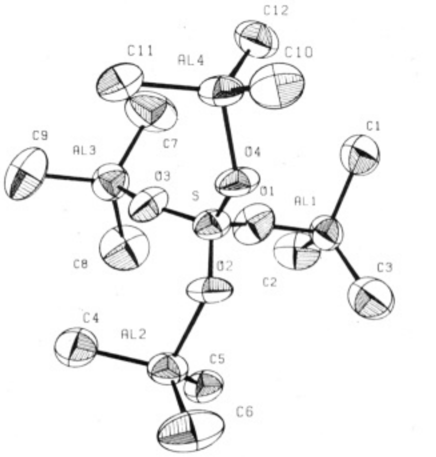

Figure 1. Structure of the $[Al_4Me_{12}SO_4]^{2-}$ anion of I.

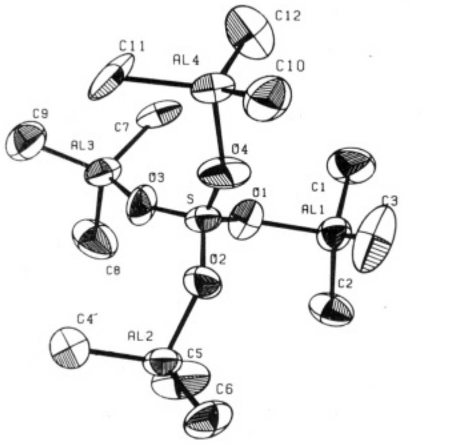

Figure 2. Structure of the $[Al_4Me_{12}SO_4]^{2-}$ anion of II.

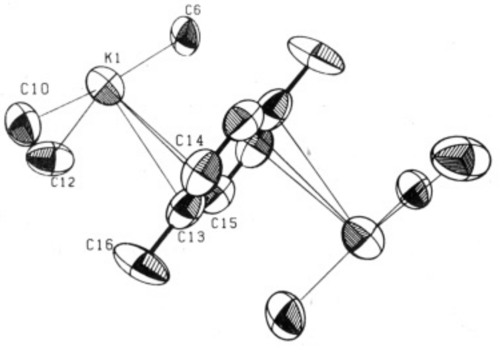

Figure 3. Packing of the *p*-xylene molecule in the lattice of II.

$[AlMe_3MeCOO]$,[13] and [K·dibenzo-18-crown-6]$[Al_2Me_6O_2]$[5] display shorter Al–O lengths of 1.871 (4), 1.83 (1), and 1.86 (1) Å, respectively.

Table I. Bond Lengths (Å) and Angles (deg) for $K_2[Al_4Me_{12}SO_4]$

	I	II
Bond Lengths		
S-C(1)	1.44 (1)	1.452 (8)
S-O(2)	1.47 (1)	1.462 (8)
S-O(3)	1.48 (1)	1.453 (9)
S-O(4)	1.481 (8)	1.437 (9)
Al(1)-O(1)	1.88 (1)	1.977 (9)
Al(1)-C(1)	1.93 (2)	1.98 (1)
Al(1)-C(2)	1.98 (2)	2.03 (1)
Al(1)-C(3)	1.93 (2)	1.93 (2)
Al(2)-O(2)	1.908 (9)	1.889 (9)
Al(2)-C(4)	1.94 (2)	1.94 (1)
Al(2)-C(5)	1.96 (1)	1.95 (1)
Al(2)-C(6)	1.97 (2)	1.95 (1)
Al(3)-O(3)	1.92 (1)	1.89 (1)
Al(3)-C(7)	1.96 (2)	1.98 (2)
Al(3)-C(8)	1.96 (2)	1.98 (2)
Al(3)-C(9)	1.95 (2)	1.95 (2)
Al(4)-O(4)	1.909 (8)	1.886 (9)
Al(4)-C(10)	1.98 (2)	1.95 (1)
Al(4)-C(11)	1.97 (2)	1.97 (1)
Al(4)-C(12)	1.95 (2)	1.94 (2)
Bond Angles		
O(1)-S-O(2)	109.8 (6)	110.0 (5)
O(1)-S-O(3)	111.3 (7)	108.0 (5)
O(2)-S-O(3)	110.8 (6)	109.7 (5)
O(1)-S-O(4)	109.5 (6)	109.9 (6)
O(2)-S-O(4)	103.9 (6)	106.9 (6)
O(3)-S-O(4)	111.3 (5)	112.4 (5)
O(1)-Al(1)-C(1)	102.1 (6)	98.5 (6)
O(1)-Al(1)-C(2)	101.7 (7)	100.7 (5)
C(1)-Al(1)-C(2)	114.1 (8)	114.1 (7)
O(1)-Al(1)-C(3)	105.4 (7)	106.4 (5)
C(1)-Al(1)-C(3)	116.5 (9)	118.0 (8)
C(2)-Al(1)-C(3)	114.6 (7)	115.4 (7)
O(2)-Al(2)-C(4)	104.1 (5)	104.4 (5)
O(2)-Al(2)-C(5)	105.3 (6)	107.8 (6)
C(4)-Al(2)-C(5)	115.2 (7)	114.0 (8)
O(2)-Al(2)-C(6)	100.0 (6)	99.0 (5)
C(4)-Al(2)-C(6)	112.2 (9)	114.4 (6)
C(5)-Al(2)-C(6)	117.5 (7)	115.2 (7)
O(3)-Al(3)-C(7)	103.5 (8)	102.7 (5)
O(3)-Al(3)-C(8)	103.8 (7)	101.8 (6)
C(7)-Al(3)-C(8)	115.9 (9)	116.9 (6)
O(3)-Al(3)-C(9)	96.9 (8)	101.0 (6)
C(7)-Al(3)-C(9)	117.5 (9)	116.0 (6)
C(8)-Al(3)-C(9)	115.1 (8)	114.8 (7)
O(4)-Al(4)-C(10)	99.2 (6)	100.4 (5)
O(4)-Al(4)-C(11)	106.4 (5)	104.8 (6)
C(10)-Al(4)-C(11)	112.8 (8)	114.9 (7)
O(4)-Al(4)-C(12)	106.3 (5)	102.6 (6)
C(10)-Al(4)-C(12)	115.1 (8)	118.1 (7)
C(11)-Al(4)-C(12)	115.1 (8)	113.3 (7)
S-O(1)-Al(1)	155.6 (9)	131.8 (5)
S-O(2)-Al(2)	136.7 (7)	139.3 (6)
S-O(3)-Al(3)	140.1 (7)	144.8 (6)
S-O(4)-Al(4)	136.6 (7)	150.5 (7)

The environment around the sulfate ion appears crowded. The best indicators of this are the S–O–Al bond angles: in I they range from 137 to 156° and average 142° and in II, from 132 to 150° and average also 142°. These are the largest values yet seen for E–O–Al angles in related systems. The average values are 137° in $[NMe_4]$-$[AlMe_3MeCOO]$,[13] 136° in $[NMe_4][Al_2Me_6MeCOO]$,[7] 124° in $K[Al_2Me_6NO_3]$,[4] 123° in $K[AlMe_3NO_3]\cdot C_6H_6$,[4] and 123° in [K·dibenzo-18-crown-6]$[AlMe_3NO_3]\cdot 0.5C_6H_6$.[12] The parameters of the SO_4^{2-} itself are normal. The O–S–O angles are 109° in both I and II, and the S–O lengths, 1.47 (2) Å in I and 1.45 (1) Å in II, are close to the 1.469 Å value found in the low-temperature form of K_2SO_4.[14]

The mode of packing of the potassium ions in the lattice is of importance. It has previously been noted that the cation environment may lie at the basis of the liquid clathrate effect.[3] Indeed, numerous packing anomalies have been found in related structures. In $K[Al_2Me_6N_3]$ there are two independent potassium environments, one in which there are close K···N contacts and one with K ions packed among methyl groups.[15] The same situation was found in $K[Al_2Me_6NO_3]$. In I and II, there are also two crystallographically different potassium ions. For I, K(1)

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Table II. Potassium Ion Environment in I and II

I		II	
K(1)-C(3)[a]	3.64 (2)	K(1)-C(4)[f]	3.11 (1)
K(1)-C(4)	3.21 (2)	K(1)-C(6)	3.23 (1)
K(1)-C(5)[b]	3.25 (2)	K(1)-C(7)[g]	3.58 (2)
K(1)-C(10)[b]	3.37 (1)	K(1)-C(10)	3.19 (1)
K(1)-C(12)[c]	3.11 (2)	K(1)-C(12)[g]	3.26 (2)
K(2)-O(2)[d]	3.01 (1)	K(1)-C(13)	3.33 (2)
K(2)-O(4)[d]	2.91 (1)	K(1)-C(14)	3.45 (2)
K(2)-C(2)[c]	3.27 (2)	K(1)-C(15)	3.49 (2)
K(2)-C(6)[e]	3.36 (2)	K(2)-O(1)[h]	3.024 (9)
K(2)-C(10)	3.38 (2)	K(2)-C(1)[h]	3.52 (2)
K(2)-C(11)[d]	3.19 (2)	K(2)-C(2)	3.43 (2)
		K(2)-C(5)	3.49 (1)
		K(2)-C(7)[h]	3.40 (1)
		K(2)-C(8)[h]	3.43 (2)
		K(2)-C(11)[g]	3.24 (2)

[a] Atoms related to those in Table IV by $(-x, {}^1/_2 + y, {}^1/_2 - z)$. [b] $(-x, 1 - y, -z)$. [c] $(1 - x, {}^1/_2 + y, {}^1/_2 - z)$. [d] $(1 - x, 1 - y, 1 - z)$. [e] $(1 + x, y, z)$. [f] Atoms related to those in Table V by $(1 - x, 2 - y, 1 - z)$. [g] $(x, {}^3/_2 - y, z - {}^1/_2)$. [h] $(1 - x, 1 - y, 1 - z)$.

Table III. Crystal Data and Summary of Intensity Data and Structure Refinement

	$K_2[Al_4Me_{12}SO_4]$	$K_2[Al_4Me_{12}SO_4]\cdot$ 0.5*p*-xylene
mol wt	462.6	515.7
space group	$P2_1/c$	$P2_1/c$
cell constants		
a, Å	10.223 (4)	9.773 (3)
b, Å	20.225 (7)	15.497 (6)
c, Å	14.039 (4)	20.442 (9)
β, deg	112.20 (3)	92.51 (3)
cell vol, Å^3	2687.5	3093.0
molecules/unit cell	4	4
D(calcd), g cm^{-3}	1.14	1.11
μ(calcd), cm^{-1}	5.19	5.00
radiation	Mo Kα	Mo Kα
max cryst dimens, mm	0.75 × 0.13 × 0.75	0.23 × 0.30 × 0.65
scan width	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ
std reflctns	200, 400	040, 008
variatn of std	±2%	±2%
reflctns measd	3369	2572
2θ range, deg	4-42	4-36
reflctns collected	1576	1300
no. of parameters varied	208	244
GOF	2.4	0.54
R	0.095	0.055
R_w	0.093	0.059

Table IV. Final Fractional Coordinates for $K_2[Al_4Me_{12}SO_4]$, I

atom	*x/a*	*y/b*	*z/c*
K(1)	0.2330 (6)	0.6522 (2)	0.1078 (3)
K(2)	0.7575 (4)	0.5876 (2)	0.4475 (4)
S	0.2810 (4)	0.3731 (2)	0.3123 (3)
Al(1)	0.1521 (5)	0.2277 (2)	0.2339 (4)
Al(2)	0.0110 (4)	0.4635 (2)	0.2401 (4)
Al(3)	0.3981 (5)	0.4172 (3)	0.1403 (4)
Al(4)	0.5746 (4)	0.3581 (2)	0.4971 (3)
O(1)	0.234 (1)	0.3122 (5)	0.2573 (8)
O(2)	0.1606 (8)	0.4074 (5)	0.3231 (7)
O(3)	0.3515 (9)	0.4159 (5)	0.2606 (7)
O(4)	0.3758 (8)	0.3585 (5)	0.4196 (6)
C(1)	0.312 (2)	0.1716 (9)	0.305 (1)
C(2)	0.082 (2)	0.2214 (9)	0.082 (1)
C(3)	0.006 (2)	0.2305 (9)	0.289 (1)
C(4)	0.107 (2)	0.5369 (8)	0.205 (1)
C(5)	−0.105 (1)	0.4085 (8)	0.124 (1)
C(6)	−0.071 (2)	0.489 (1)	0.342 (1)
C(7)	0.529 (2)	0.343 (1)	0.162 (2)
C(8)	0.215 (2)	0.407 (1)	0.026 (1)
C(9)	0.477 (2)	0.506 (1)	0.159 (1)
C(10)	0.573 (1)	0.3502 (8)	0.637 (1)
C(11)	0.646 (1)	0.4441 (9)	0.473 (1)
C(12)	0.649 (2)	0.2817 (8)	0.450 (1)

Table V. Final Fractional Coordinates for $K_2[Al_4Me_{12}SO_4]\cdot 0.5p$-xylene, II

atom	*x/a*	*y/b*	*z/c*
K(1)	0.1783 (4)	0.9896 (2)	0.3679 (2)
K(2)	0.5206 (4)	0.5349 (2)	0.3737 (2)
S	0.3363 (4)	0.7188 (2)	0.6381 (2)
Al(1)	0.1653 (5)	0.5739 (3)	0.5650 (2)
Al(2)	0.4900 (5)	0.8036 (3)	0.5224 (2)
Al(3)	0.5817 (5)	0.6582 (3)	0.7351 (2)
Al(4)	0.1375 (4)	0.7916 (3)	0.7466 (2)
O(1)	0.3124 (9)	0.6294 (5)	0.6195 (4)
O(2)	0.3523 (9)	0.7715 (6)	0.5797 (4)
O(3)	0.4610 (9)	0.7224 (6)	0.6794 (4)
O(4)	0.220 (1)	0.7520 (6)	0.6704 (4)
C(1)	0.120 (2)	0.479 (1)	0.6255 (7)
C(2)	0.272 (2)	0.5355 (9)	0.4871 (7)
C(3)	0.028 (2)	0.662 (1)	0.5467 (8)
C(4)	0.616 (2)	0.8735 (9)	0.5757 (7)
C(5)	0.571 (2)	0.6983 (9)	0.4894 (7)
C(6)	0.378 (1)	0.8685 (9)	0.4585 (6)
C(7)	0.460 (2)	0.570 (1)	0.7714 (6)
C(8)	0.718 (2)	0.618 (1)	0.6734 (8)
C(9)	0.648 (2)	0.747 (1)	0.7957 (7)
C(10)	−0.009 (1)	0.863 (1)	0.7079 (6)
C(11)	0.283 (2)	0.856 (1)	0.7951 (6)
C(12)	0.088 (2)	0.685 (1)	0.7890 (8)
C(13)	−0.106 (2)	0.987 (2)	0.4515 (8)
C(14)	−0.064 (2)	1.070 (1)	0.470 (1)
C(15)	−0.045 (3)	0.918 (1)	0.485 (1)
C(16)	−0.226 (2)	0.974 (1)	0.4015 (9)

has five contacts with methyl carbon atoms out to 3.7 Å (Table II), while K(2) has two close oxygen contacts at 2.91 (1) and 3.01 (1) Å. In II the *p*-xylene molecules play an important role. As is shown in Figure 3, the aromatic molecule is positioned about a crystallographic center of inversion and thus "bridges" (or "insulates") K(1) and its symmetry mate. This type of cation···aromatic interaction has been observed in [K·dibenzo-18-crown-6]-$[Al_2Me_6O_2]\cdot 1.5C_6H_6$.[5] K(2) has a close oxygen contact at 3.024 (9) Å.

Experimental Section

All reactions were carried out under a nitrogen atmosphere by using Schlenk techniques or an inert atmosphere box. Solvents were dried and degassed in the normal manner.

Preparation of $K_2[Al_4Me_{12}SO_4]$, I, and $K_2[Al_4Me_{12}SO_4]\cdot 0.5p$-xylene, II. To a suspension of 0.01 mol of K_2SO_4 in 25 mL of toluene was added 0.04 mol of $AlMe_3$. The resulting mixture was heated for 12 h at 100 °C, and a liquid clathrate of composition $K_2[Al_4Me_{12}SO_4]\cdot n$ toluene resulted in quantitative yield. Slow cooling to room temperature afforded single crystals of the unsolvated I. This procedure was repeated in *p*-xylene, and the solvate II resulted.

X-ray Data Collection and Structure Determination for $K_2[Al_4Me_{12}SO_4]$, I. Single crystals of I were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 40°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table III. Intensity data were recorded on the diffractometer in the usual manner.[16] All reflections in an independent quadrant out to $2\theta = 42°$ were measured; 1576 reflections were considered observed $[I > 3\sigma(I)]$. The intensities were corrected for Lorentz and polarization effects but not for absorption (because of the low linear

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(16) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 46.

absorption coefficient and the orientation of the crystal during data collection, the maximum range of transmission factors was from 0.77 to 0.88).

Absences in $0k0$ of $k = 2n + 1$, and $h0l$, $l = 2n + 1$, uniquely defined the space group to be $P2_1/c$. The structure was solved by the straightforward application of the direct methods program MULTAN.[17] Several cycles of least-squares refinement of the positional and isotropic thermal parameters of the non-hydrogen atoms afforded a reliability index of $R_1 = (|F_o| - |F_c|)/|F_o| = 0.18$. Conversion to anisotropic thermal parameters and further refinement gave $R_1 = 0.12$. The 36 hydrogen atom positions were determined from a difference Fourier map, but their parameters were not refined. More cycles of refinement led to final values of $R_1 = 0.095$ and $R_2 = \{w(|F_o| - |F_c|)^2/(F_o)^2\}^{1/2} = 0.090$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference Fourier showed no feature greater than 0.4 e/Å^3. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted.

Full-matrix, least-squares refinement was carried out by using the SHELX Library.[18] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for K, S, Al, C, and O were taken from Cromer and Waber;[19] those for H were from ref 20. The final values of the positional parameters are given in Table IV.[21]

X-ray Data Collection and Structure Determination for $K_2[Al_4Me_{12}SO_4]\cdot 0.5p$-xylene, II. Data collection, structure solution, and refinement were carried out in the same manner as I. One independent quadrant of reflections was measured out to $2\theta = 36°$ resulting in 1300 observed (very little scattering was found beyond $2\theta = 36°$). R_1 with all non-hydrogen atoms refined isotropically was 0.108. Conversion to anisotopic thermal parameters and further refinement gave $R_1 = 0.069$.

All H atoms were located from a difference Fourier, but their parameters were not refined. Final refinement gave $R_1 = 0.055$ and $R_2 = 0.059$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviation. A final difference Fourier showed no feature greater than 0.3 e/Å^3. Unit weights were used and no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)\lambda$ was noted. The final values of the positional parameters are given in Table V.[21]

Acknowledgment. We are grateful to the National Science Foundation and the University of Alabama School of Mines and Energy Development for support of this work.

Registry No. I, 87861-92-5; II, 87861-93-6; K_2SO_4, 7778-80-5; $AlMe_3$, 75-24-1.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom coordinates, complete bond lengths and angles, and structure factors for I and II (23 pages). Ordering information is given on any current masthead page.

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(19) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(20) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72.

(21) See paragraph at the end of paper regarding supplementary material.

Halide, Hydride, and Alkyl Derivatives of (Pentamethylcyclopentadienyl)bis(trimethylphosphine)ruthenium[†]

T. Don Tilley,[‡] Robert H. Grubbs,*[§] and John E. Bercaw*[§]

Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125, and Chemische Laboratorien der Eidgenossische Technische Hochschule, Zurich, Switzerland

Received July 22, 1983

The reaction of ruthenium trichloride with pentamethylcyclopentadiene (C_5Me_5H), followed by PMe_3 gives $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$. Reaction of (pentamethylcyclopentadienyl)bis(trimethylphosphine)ruthenium chloride with the Grignard reagents RMgX affords alkyl derivatives (R = Me, Et, CH_2CMe_3, or CH_2SiMe_3) or the hydride $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2H$ (R = *t*-Bu or *i*-Pr). The complexes $(\eta^5\text{-}C_5Me_5)_2Ru$, $(\eta^5\text{-}C_5Me_5)Ru(NBD)Cl$ (NBD = norbornadiene), and $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Br$ are also reported. Routes to the cationic species $[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(CO)][PF_6]$ and $[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2HCl][PF_6]$ are described.

Introduction

Attention is currently being drawn to the fact that more basic, electron-donating ligands significantly modify the chemistry of group 8 metals. This has been most amply demonstrated with the trimethylphosphine (PMe_3) and pentamethylcyclopentadienyl (C_5Me_5) ligands. One aspect of the change in reactivity in going to more electron-rich noble metal complexes appears to be the stabilization of higher formal oxidation states. Consequently, organometallic ruthenium(IV) derivatives such as $(\eta^5\text{-}C_5Me_4Et)Ru(CO)Br_3$[1] and $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2XCl][PF_6]$ (X = H and Cl)[2] have recently been characterized. In other cases, these electron-rich metal centers have allowed isolation of new types of ligand arrays, which are likely to be less stable in the presence of poorer, more labile donors

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[†] Contribution No. 6869 from the Laboratories of Chemistry, California Institute of Technology.

[‡] Chemische Laboratorien der Eidgenossische Technische Hochschule.

[§] California Institute of Technology.

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