they would be about 3.70 Å. Here, then, is an interesting and worthwhile synthetic challenge, whereby predictions made before the fact could be tested experimentally.

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Registry No. 1, 99797-57-6; **2**, 99808-51-2; **3**, 99797-58-7; $Ta_2Cl_6(THT)_3$, 66758-43-8; $K_4Mo_2Cl_6$, 25448-39-9; $Ru_2Cl(O_2CCH_3)_2(mhp)$, 96825-40-0; $HC(PPh_2)_3$, 28926-65-0.

Supplementary Material Available: Full list of bond distances and angles, tables of anisotropic displacement parameters, and listing of observed and calculated structure factors for all three compounds (41 pages). Ordering information is given on any current masthead page.

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Structural Correlations between the Tetraisopropylphosphonium Cation and Triisopropylphosphonium Isopropylide: An X-ray Diffraction Study[†]

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Abstract: Tetraisopropylphosphonium iodide (**1a**) and tetraphenylborate (**1b**) were prepared in a three-step synthesis from triisopropylphosphine. Single-crystal X-ray diffraction data were collected for both salts, but only the structure of **1b** could be solved. Crystals of **1b** are orthorhombic, space group $P2_12_12$, $a = 9.415$ (1) Å, $b = 15.199$ (2) Å, $c = 11.157$ (1) Å, $V = 1596.6$ Å^3, $Z = 2$, and $R_w = 0.063$ for 181 parameters and 2519 observed reflections ($F_o \geqslant 4.0\sigma(F_o)$). Both the tetraisopropylphosphonium cations and the tetraphenylborate anions lie on a crystallographic twofold axis, but the actual cation symmetry approaches point group S_4 ($\bar{4}$) symmetry, in agreement with theoretical predictions for tetrahedral species with four ligands of $C_s(m)$ symmetry. The isopropyl groups are rotated pairwise in opposite directions (C1,C1*/C2,C2*) by 110° (av) away from the fully staggered $D_{2d}(\bar{4}2m)$ conformation. The triisopropylphosphonium isopropylide (**2**), obtained from **1a** and $NaNH_2$ in liquid ammonia, crystallizes in triclinic needles, space group $P\bar{1}$, $a = 7.587$ (2) Å, $b = 8.030$ (2) Å, $c = 11.521$ (2) Å, $\alpha = 86.17$ (2)°, $\beta = 106.08$ (2)°, $\gamma = 104.66$ (2)°, $V = 652.5$ Å^3, $Z = 2$, and $R_w = 0.055$ for 154 parameters and 1654 observables. The individual ylide molecules have approximate $C_s(m)$ symmetry, but the phosphorus-carbon skeleton is clearly reminiscent of a parent $D_{2d}(\bar{4}2m)$ symmetry. The relatively long ylidic bond P–C1 is complemented by the short aliphatic P–C4 bond. Distortions also arise from a large C—P═C angle (C3—P—C1). The ylidic carbon atom C1 exhibits a pyramidal configuration. Through these effects, the steric interactions are reduced with retention of the basic symmetry. No intra- or intermolecular hydrogen bonds between carbon atoms are present, which could account for the facile proton transfer observed in solution.

Predictions of ground-state conformations of simple molecules must often remain unconfirmed by experimental evidence, even for a number of seemingly trivial cases. It was only recently, e.g., that species with four *tert*-butyl groups attached to a central atom could be synthesized and structurally characterized, resulting in a clear corroboration of the $T(23)$ symmetry proposed on the basis of force-field calculations.[1] In the tetra-*tert*-butylphosphonium cation, the possible extreme point group symmetry $T_d(\bar{4}3m)$ is reduced to $T(23)$ through a conrotatory distortion of all *four threefold rotors* (CC_3) by 14° and a concomitant rotation of all CH_3 rotors by 11°. Both values are in excellent agreement with the theoretical figures.[2]

The problem of *four twofold rotors* of $C_{2v}(mm)$ symmetry at a common central atom could be solved experimentally with much less difficulty, since a whole series of tetraphenylated molecules with physical properties more amenable to the structural determination was readily available.[3] And yet a consistent picture was only emerging after careful consideration of the special features of individual systems.[4] (See also below, where the structure of the BPh_4^- anion is reconsidered.)

Even less straightforward, both in theory and experiment, has been the approach to the conformation of four ligands with *mirror symmetry* (point group C_s/m) at a common central atom. A case in question was the crystal structure of tetracyclohexylsilane,[5] which was brought in line with the existing body of information only after detailed scrutiny of the molecular parameters.[6] Another example from the current literature is the evaluation of crystal structures of compounds of the pentaerythrole type, $C(CH_2X)_4$. The functionalities associated with X = OH, NH_2, etc., can impose strong intermolecular interactions in these materials, however, originating from dipole moments, hydrogen bonds, or other specific contacts with corresponding structural consequences.[7]

As a continuation of the work on $(t\text{-Bu})_4P^+$, it was therefore decided to investigate the structure of a phosphonium cation bearing four *isopropyl* groups, the simplest carbon skeleton of $C_s(m)$ symmetry. This cation $[(CH_3)_2CH]_4P^+$, **1**, was recently

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[†] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the numbering: e.g., III → 3 and 13.)

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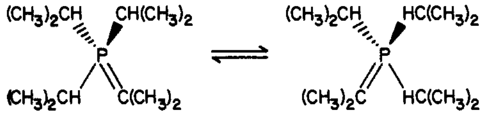
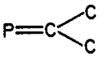
0002-7863/86/1508-0976$01.50/0

Scheme I



prepared and characterized spectroscopically,[8] but no structural data were available. We are also not aware of structural work on any other $(i\text{-Pr})_4M$ species. A study of $(i\text{-Pr})_4Si$ by electron diffraction is under way.[9]

A second complex with unsolved problems of structure and conformation has been the simple *trialkylphosphonium ylides*.[10] Though a number of tri*aryl*phosphonium homologues with various substituents at the ylidic function have been carefully studied,[10] the alkyl series is much less well represented.[11,12] Methylide structures of $R_3P{=}CH_2$ suffer from the inaccuracies associated with the localization of the $P{=}CH_2$ hydrogen atoms both by X-ray and electron diffraction.[11-13] Only the determination of an *isopropylidene* with its minimum carbon skeleton



would be free of these uncertainties. The determination of the crystal structure of triphenylphosphonium isopropylide $[(C_6H_5)_3P{=}C(CH_3)_2]$ has been announced in the literature, but details have never appeared.[14]

Owing to irreversible isomerization processes involving rapid protron transfer,[15] isopropylides with methyl, ethyl, or *n*-propyl groups attached to phosphorus are not available.[16] The first stable trialkylphosphonium isopropylide therefore appears to be the title compound $(i\text{-Pr})_3P{=}C(CH_3)_2$, **2**, for which a "proton scrambling" leads to reproduction of identical species (Scheme I). This process is rapid in solution already at room temperature, especially in the presence of minute amounts of a protic catalyst,[16] suggesting a facile intra- and/or intermolecular proton shift.[15-19] It was not inconceivable that C–H···C hydrogen bonds were involved, and for this point alone, a definite structure determination was of prime interest.

Tetraisopropylphosphonium Iodide and Tetraphenylborate

The tetraisopropylphosphonium cation $[(CH_3)_2CH]_4P^+$ is difficult to synthesize through direct quaternization of triisopropylphosphine with an isopropyl halide. Due to steric effects, this reaction is an extremely slow process. A "buildup" of the fourth isopropyl group is therefore the method of choice. The three-step procedure according to eq 1 gives good yields in a reasonable period of time.

$$i\text{-Pr}_3P \xrightarrow{EtX} [i\text{-Pr}_3PEt]X \xrightarrow{base} i\text{-Pr}_3P{=}CHMe \xrightarrow{MeI} \underset{\mathbf{1a}}{[i\text{-Pr}_4P]I}$$

$$\mathbf{1a} \xrightarrow{Na[BPh_4]} \underset{\mathbf{1b}}{[i\text{-Pr}_4P]BPh_4} \qquad (1)$$

The *iodide* **1a** thus obtained crystallizes in a body-centered tetragonal space group (Laue symmetry $4/m$, see Experimental Section and Table I). Both the phosphorus and the iodine atoms are at alternating sites along the crystallographic *c* axis, viz., 0, 0, 0 and 0, 0, 0.5. It was not yet possible to determine the positions of the carbon atoms, however.

1a was therefore converted into the tetraphenylborate **1b**, which crystallized in colorless needles from acetone in the orthorhombic space group $P2_12_12$ (no. 18). The structure determination of this compound was straightforward (Table I) and gave the expected arrangement of columns of stacked cations and anions running again parallel to the crystallographic *c* axis (Figure 1).

A similar arrangement is found in the crystal of a large variety of other tetrasubstituted molecules and ions, of which the tetra-

Table I. Crystallographic Data for **1a**, **1b**, and **2**

	compound		
	1a	**1b**	**2**
formula	$C_{12}H_{28}IP$	$C_{36}H_{48}BP$	$C_{12}H_{27}P$
fw	330.23	522.57	202.32
space group	*a*	$P2_12_12$	$P\bar{1}$
a, Å	7.749 (3)	9.415 (1)	7.587 (2)
b, Å	7.749 (3)	15.199 (2)	8.030 (2)
c, Å	12.840 (4)	11.157 (1)	11.521 (2)
a, deg	90.00	90.00	86.17 (2)
β, deg	90.00	90.00	106.08 (2)
γ, deg	90.00	90.00	104.66 (2)
V, Å³	771.0	1596.6	652.5
Z	2	2	2
d_{calcd}, g/cm³	1.422	1.087	1.030
μ(Mo Kα), cm⁻¹	21.30	1.03	1.68
F(000)	336	568	228
T, °C	−40	+21	−40
diffractometer	Syntex $P2_1$	CAD4	Syntex $P2_1$
radiation	Mo Kα	Mo Kα	Mo Kα
λ, Å	0.710 69	0.710 69	0.710 69
scan mode	ω	ω − 2θ	ω
scan width (in ω), deg	1.2	0.5 + 0.35 tan θ	0.9
scan rate (in ω), deg/min	0.9–29.3	1–10	0.9–29.3
std refl.	110	$0\bar{1}4,332,\bar{1}41$	$1,\bar{2},\bar{2}$
$(\sin\theta/\lambda)_{max}$, Å⁻¹	0.572	0.648	0.572
hkl range	8,8,14	±12,19,14	8,±9,±13
refl. measd	746	3947	2047
refl. unique	609	3620	2047
R_{int}	*a*	0.013	
refl. obsd	*a*	2519	1654
param. ref	*a*	181	154
$(shift/error)_{max}$	*a*	0.04	0.002
R^b	*a*	0.045	0.049
$R_w{}^c$	*a*	0.063	0.055
$\Delta\rho_{fin.}$(max), e/Å³	*a*	0.24	0.34

[a] See Experimental Section. [b] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$. The anisotropic temperature factors were of the form: $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$.

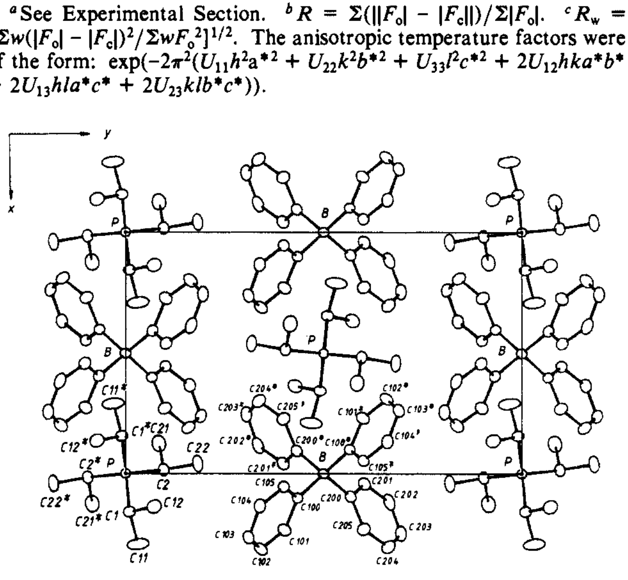


Figure 1. View of the unit cell of **1b** in the projection down the crystallographic *c* axis and atomic numbering scheme used. Starred atoms are related to those without an asterisk by the twofold crystallographic axis which is perpendicular to the plane of the paper. H atoms omitted for clarity (ORTEP, thermal ellipsoids at the 20% probability level).

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phenylated species are particularly well-documented. $S_4(\bar{4})$ molecular symmetry was found to be predominant. The structural relationships between **1b** and the thoroughly investigated tetraphenyl-substituted group VB (5) onium salts deserves comment. The majority of the latter were found to crystallize in the tetragonal space group $I\bar{4}$ (no. 82) if the counterions are likewise tetrahedrally substituted.[20] Both the cations and the anions were shown to be of crystallographic $S_4(\bar{4})$ symmetry. For counterions of lower symmetry, notably twofold rotational symmetry, crystallographic subgroups of $I\bar{4}$, as, e.g., $I2$,[21] were shown to account for the symmetry reduction.

Although the space group $P2_12_12$ of **1b** does not obey a group/subgroup relationship with $I\bar{4}$, similarities in the crystal packing are immediately obvious. As can be seen from the plot of a cell projection down the crystallographic *c* axis (Figure 1), the actual arrangement of the columns of stacked cations and anions is not much different from that in the more symmetrical, body-centered tetragonal case $I\bar{4}$. In particular, the pseudo-body-centering of the cation and anion columns in the projection is most conspicuous. Differences arise, however, from the reduction in actual symmetry to $C_2(2)$, in the inequality of the crystallographic *a* and *b* axes, and, most notably, from the different relative height in *c* of the cations and anions in the different columns. Inspection of Figure 1 gives also hints as to the probable origin of this unexpected reduction of symmetry. Close proximity of the phenyl rings of the different tetraphenylborate anions seem to "spread" the *b* axis. Futhermore, it should be noted that isopropyl groups residing in "pockets" of the tetraphenylborates seem to influence the C–B–C angles and thus the anion geometry (see below). In **1b**, both the $(i\text{-Pr})_4P^+$ and the BPh_4^- ions lie on a crystallographic twofold axis, but the structure of the cation is clearly approaching the higher point group $S_4(\bar{4})$, thus exceeding the crystallographically imposed $C_2(2)$ symmetry and illustrating nicely the group/subgroup relationship of $S_4(\bar{4})$ and $C_2(2)$. As shown in Figure 1, the line bisecting the angles C1–P–C1* and C2–P–C2* (perpendicular to the plane of the paper) is not only a $C_2(2)$ but also to a good approximation an $S_4(\bar{4})$ axis. This symmetry argument can be supported by the bond distances and angles and especially the torsional angles given in Table IIa. The discrepancies between P–C1 and P–C2 are quite small, as are those between C1–P–C1* and C2–P–C2* or between C1–P–C2* and C1–P–C2, respectively. The respective deviations are close to or within the standard errors of the experiment.

In principle, the $(i\text{-Pr})_4P^+$ cation could adopt a symmetry as high as $D_{2d}(\bar{4}2m)$ if the isopropyl groups were rotated into positions where the hydrogen atoms of the methine groups lie in the same plane with the corresponding C1–P–C1* or C2–P–C2* sets.[22] These planes would then be mirror planes for the methyl groups and, of course, contain the fourfold inversion axis. In the cation of **1b**, the isopropyl groups are rotated out of this unique position in that two-by-two sets are moved in opposite directions (clockwise and counterclockwise, respectively) by 104–116° (av 110°) (Table IIa). From the difference between the torsional angles which should be equivalent for an $S_4(\bar{4})$ molecular symmetry, the overall deviation from the latter may be estimated to be at most 5° (Table IIa). This torsional motion is equivalent to the distortions induced in the $(t\text{-Bu})_4P^+$ cations mentioned in the Introduction section, which reduces the $T_d(\bar{4}3m)$ symmetry to point group $T(23)$. Both effects are in line with force-field calculations for these topologies.[2,4,6] This result is of great significance in that it confirms earlier predictions that species with four $C_s(m)$ ligands at a tetrahedrally coordinated central atom should adopt $S_4(\bar{4})$ symmetry. The geometrical situation in tetracyclohexylsilane is exactly equivalent as far as crystallographic site symmetry and actual molecular symmetry are concerned. It should be noted, however, that the degree of alkyl group twisting from the maximum attainable $D_{2d}(\bar{4}2m)$ is far less (7–8°) for the cyclohexyl case. As the latter forms a molecular crystal with only one type of molecule, whereas **1b** is composed of two very different ionic components, it appears that the $S_4(\bar{4})$ symmetry rule is indeed valid even under very different conditions of stoichiometry and structure.

Table II. (a) Selected Interatomic Distances [Å], Angles, and Torsional Angles (deg) in the Cation $[(i\text{-Pr})_4P]^+$ of Compound **1b**. (See Figure 1 for Numbering Scheme Adopted.) Values in Brackets Indicate the Difference between the Idealized Value for the All-Staggered $D_{2d}(\bar{4}2m)$ Conformation and the Observed One. (b) Selected Interatomic Distances [Å], Angles, and Torsional Angles [deg] in the Anion $[BPh_4]^-$ of Compound **1b**

	a		
P–C1	1.836 (2)	C1–P–C2*	110.4 (1)
P–C2	1.823 (2)	C1–P–C2	110.9 (1)
C1–C11	1.511 (4)	C1–P–C1*	106.9 (1)
C1–C12	1.523 (4)	C2–P–C2*	107.4 (2)
C2–C21	1.528 (3)	P–C1–C11	112.8 (2)
C2–C22	1.526 (3)	P–C1–C12	114.1 (2)
		P–C2–C21	113.5 (2)
		P–C2–C22	113.9 (2)
C1–P–C2–C21	167.8	C11–C1–C12	110.7 (2)
C2–P–C1–C11	−51.0	C21–C2–C22	111.4 (2)
C1–P–C2–C22	−63.3		
C2–P–C1–C12	76.5		
C(1)–P–C(1)*–C(11)*	−171.4	[111.4]	
C(1)–P–C(1)*–C(12)*	−44.0	[104.0]	
C(1)–P–C(1)*–H(1)*	71.8	[108.2]	
C(2)–P–C(2)*–C(22)*	176.0	[116.0]	
C(2)–P–C(2)*–C(21)*	47.1	[107.1]	
C(2)–P–C(2)*–H(2)*	−66.4	[113.6]	
	b		
B–C(100)	1.649 (3)	C(100)–B–C(200)*	103.6 (1)
B–C(200)	1.641 (3)	C(200)–B–C(200)*	111.9 (2)
		C(100)–B–C(100)*	112.8 (2)
		C(100)–B–C(200)	112.6 (1)
C(100)–B–C(100)*–C(101)*	−151.8		
C(100)–B–C(100)*–C(105)*	35.0		
C(200)–B–C(200)*–C(205)*	−148.3		
C(200)–B–C(200)*–C(201)*	37.2		
C(100)–B–C(200)–C(201)	153.5		
C(100)–B–C(200)–C(205)	−32.0		
C(200)–B–C(100)–C(105)	151.9		
C(200)–B–C(100)–C(101)	−35.0		
C(100)–B–C(200)*–C(201)*	−84.4		
C(100)–B–C(200)*–C(205)*	90.2		
C(200)–B–C(100)*–C(101)*	86.2		
C(200)–B–C(100)*–C(105)*	−87.0		

The P–C1 and P–C2 distances in compound **1b** reflect the steric crowding in the cation. They are significantly longer than standard dimensions of methylphosphorus compounds but, naturally, shorter than in the overcrowded *tert*-butyl homologues. The distances can also serve as an important reference for the values of the corresponding ylide **2** (below). Again for steric reasons, the PCC angles are greater than the tetrahedral angle, whereas CCC angles are closer to this 109° standard (Table IIa).

The geometry of the BPh_4^- anion in compound **1b** (Figure 1) also obeys crystallographic $C_2(2)$ symmetry. Close inspection of the geometrical details, especially the torsional angles, reveals that the actual molecular symmetry is higher, approaching $D_2(222)$. This is evident from the torsional angles that should be equivalent for $D_2(222)$ symmetry, as, e.g., C100–B–C100*–C101* = −151.8° and C200–B–C200*–C205* = −148.3 (Table IIb). Similarly small discrepancies are found for the torsional angles involving C105*/C201* (35.0/37.2°). The higher symmetry is also reflected in the bond angles at boron which are inconsistent with $S_4(\bar{4})$ but agree nicely with $D_2(222)$. From the differences between the equivalent torsional angles listed in Table IIb, a deviation of not larger than 6° from $D_2(222)$ symmetry may be derived. It should be kept in mind that $D_2(222)$ again is a subgroup of the parent $D_{2d}(\bar{4}2m)$ and—in contrast to the ubiquitous $S_4(\bar{4})$ symmetry—arises by twisting the phenyl rings uniformly in *one*

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[20] Müller, U. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1075.

[21] Nonstandard setting of B2, *c* axis unique.

[22] Actually, two $D_{2d}(\bar{4}2m)$ conformations are conceivable. One with all P–C and C–C bonds in a staggered conformation and a second one with these bonds fully ecclipsed. Since the latter conformation suffers most from repulsive methyl group interactions, only the all-staggered alternative is considered here.

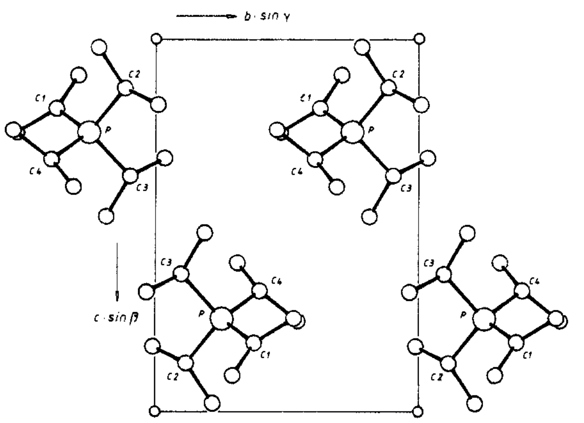


Figure 2. Projection of the unit cell contents of **2** as seen down the *a* axis (ORTEP, atoms with arbitrary radii). C1 designates the ylidic function in the molecule.

direction. Most interestingly and to the best of our knowledge, such an overall symmetry has not been observed for tetraphenyl compounds as yet.

From the packing in the unit cell (Figure 1), it appears that steric cation/anion interactions are responsible for the symmetry reduction in the anions, while the cations are much less affected.

Details of the solution of the structure and a list of final atomic coordinates and thermal parameters are given in the Experimental Section and in Table III, respectively.

Triisopropylphosphonium Isopropylide

Treatment of the tetraisopropylphosphonium iodide (**1a**) with sodium amide in liquid ammonia at −45 °C affords NaI and the ylide **2**, $(i\text{-Pr})_3P{=}C(CH_3)_2$, which crystallizes from pentane at −25 °C in the form of colorless, extremely air-sensitive needles of mp 95 °C (eq 2). The X-ray diffraction analysis (Table I)

$$\mathbf{1a} \xrightarrow{\text{NaNH}_2} \underset{\mathbf{2}}{i\text{-Pr}_3\text{P}{=}\text{CMe}_2} \qquad (2)$$

showed the product to form triclinic crystals, space group $P\bar{1}$ (no. 2), containing individual molecules in a packing pattern as depicted in Figure 2. All intermolecular distances correspond to common van der Waals' contacts, and there is no evidence for *inter*molecular hydrogen bonds or other anomalies.

With the description of ylides as zwitterionic molecules in mind, an attempt was made to detect a pairwise or collective alignment of individual dipoles ($P^+{-}C1^-$). It turned out that puckered strands of ylide molecules with the same direction of the P=C moiety are alternating with strands of those of the opposite direction, thus accounting for partial electrostatic compensation.

The individual ylide molecule **2** has no crystallographic symmetry but conforms well with $C_s(m)$ symmetry, with the mirror plane passing through atoms P, C1, C3, and H3. More important, if a projection is taken with this mirror plane perpendicular to the plane of the paper (Figure 3), the close approach to an all staggered $D_{2d}(\bar{4}2m)$ symmetry becomes immediately evident. In other words, the actual molecular symmetry of **2** is clearly derived from the ***highest possible*** (but not actual) symmetry of the parent tetraisopropylphosphonium cation (above). In **2** one of the isopropyl groups has been transformed into the ylidic function by deprotonation at C1. The concomitant planarization of C1 is also observable in **2** but it does not reach the extreme of perfect planarity. Instead, C1 is still slightly pyramidalized (Figure 4) as becomes evident from a projection of the molecule onto the C1–P–C3 plane: The sum of the angles P–C1–C11, P–C1–C12, and C11–C1–C12 is only 354.2° (Table V). This plot shows clearly that the isopropylide moiety has largely retained the parent isopropyl structure.

Figure 4 also shows that the partial planarization is the most important deviation from an all-staggered $D_{2d}(\bar{4}2m)$ symmetry, in which a mirror plane would pass through P–C2–C4, relating C1 with C3. Actually, this plane and the one through C1–P–C3 would form the set of mirror planes of point group $D_{2d}(\bar{4}2m)$. (The $S_4(\bar{4})$ axis required for the potential $D_{2d}(\bar{4}2m)$ symmetry is easily detected in Figure 3 as a normal to the plane of the paper.) It is conceivable that the lone pair of electrons of the carbanionoid atom C1 is distributed in the realm of the fourth corner of the tetrahedron (Figure 4). This lone pair is not directed toward one of the isopropyl α-hydrogen atoms, and consequently there is no indication also for *intra*molecular hydrogen bonds:

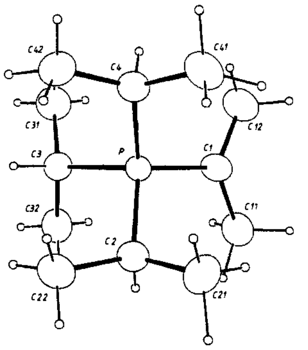


Figure 3. Molecular structure and atomic numbering scheme of **2** (ORTEP, theremal ellipsoids 50%, H atoms with arbitrary radii). A noncrystallographic mirror plane perpendicular to the plane of the paper bisects the molecule and contains atoms C3–P–C1 (see text for discussion).

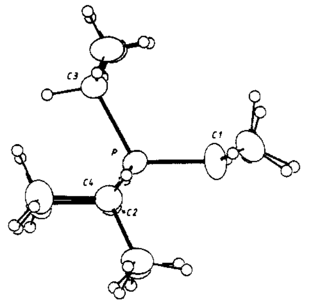
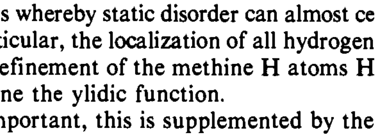


Figure 4. View of **2** perpendicular to the C1–P–C3 plane, illustrating the pyramidal configuration of the ylidic carbon atom C1 (ORTEP, thermal ellipsoids 50%, H atoms with arbitrary radii).



At this point the important question of possible disorder of the ylide molecule should be raised as some of the "distortion" might also be caused by a static disorder, making isopropyl and isopropylidene groups indistinguishable in the crystal. Fortunately, the good quality of the crystal specimen used for the structure determination allowed for a very precise determination of the molecular parameters whereby static disorder can almost certainly be ruled out. In particular, the localization of all hydrogen atoms and the successful refinement of the methine H atoms H2, H3, and H4 clearly define the ylidic function.

Probably most important, this is supplemented by the shape of the thermal ellipsoids of the C atoms. Of these, only that of C1 is indicative of slight disorder and/or a very shallow potential energy minimum of the equilibrium conformation, whereas all other tertiary C atoms behave much more isotropically. Finally, Figure 5 offers a projection roughly perpendicular to the C1–P–C4 plane. This seemingly not very meaningful view is of interest because the pertinent bond distances are another unexpected feature of the whole molecular structure (Table IV): The interatomic distance P=C1 = 1.731 (3) Å signifies a relatively long ylide bond, as standard values in other ylides tend to be shorter (around 1.70 Å). The distance P–C4 = 1.813 (3) Å, on the other hand, suggests an unusually shortened P–C single bond. Representative "internal references" are the distances P–C2 = 1.842 (3) Å and P–C3 = 1.847 (3) Å in **2**, or P–C1 = 1.836 (2) and P–C2 = 1.823 (2) Å in **1b**. Since static disorder can almost

Table III. (a) Fractional Atomic Coordinates for Tetraisopropylphosphonium Tetraphenylborate (**1b**) Esd's in Units of the Last Significant Figure in Parentheses. (b) Anisotropic Temperature Factors for **1b**

	atom	*x*	*y*	*z*
(a)	P	1.0000	0.0000	0.77936 (7)
	C1	1.1559 (2)	0.0096 (2)	0.8773 (2)
	C2	0.9837 (3)	0.0961 (2)	0.6826 (2)
	C11	1.2901 (3)	0.0316 (3)	0.8093 (3)
	C12	1.1357 (3)	0.0722 (2)	0.9826 (3)
	C21	0.8762 (4)	0.0842 (2)	0.5813 (3)
	C22	0.9588 (4)	0.1820 (2)	0.7503 (3)
	C100	0.0997 (2)	0.4341 (2)	0.7954 (2)
	C101	0.2298 (3)	0.4012 (2)	0.7563 (2)
	C102	0.3093 (3)	0.3413 (2)	0.8208 (3)
	C103	0.2613 (3)	0.3102 (2)	0.9285 (3)
	C104	0.1329 (3)	0.3388 (2)	0.9705 (3)
	C105	0.0538 (3)	0.3995 (2)	0.9043 (2)
	C200	0.0941 (3)	0.5678 (2)	0.6313 (2)
	C201	0.0421 (3)	0.6026 (2)	0.5243 (3)
	C202	0.1159 (3)	0.6655 (2)	0.4576 (3)
	C203	0.2450 (3)	0.6951 (2)	0.4955 (3)
	C204	0.3007 (3)	0.6635 (2)	0.6003 (3)
	C205	0.2272 (3)	0.6012 (2)	0.6667 (3)
	B	0.000	0.500	0.7136 (3)

	atom	*U*(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
(b)	P	0.0339 (3)	0.0346 (3)	0.0351 (3)	0	0	−0.0013 (4)
	C1	0.040 (1)	0.054 (1)	0.047 (1)	0.012 (1)	−0.0083 (9)	−0.002 (1)
	C2	0.057 (1)	0.041 (1)	0.045 (1)	0.0049 (9)	−0.011 (1)	0.003 (1)
	C11	0.045 (2)	0.177 (4)	0.070 (2)	0.020 (2)	−0.007 (1)	−0.015 (2)
	C12	0.066 (2)	0.075 (2)	0.064 (2)	−0.010 (2)	−0.022 (1)	−0.009 (2)
	C21	0.098 (2)	0.069 (2)	0.070 (2)	0.007 (2)	−0.044 (1)	0.005 (2)
	C22	0.104 (2)	0.038 (1)	0.069 (2)	0.002 (1)	−0.018 (2)	0.008 (1)
	C100	0.039 (1)	0.042 (1)	0.042 (1)	−0.006 (1)	−0.004 (1)	0.001 (1)
	C101	0.054 (1)	0.062 (1)	0.051 (1)	−0.008 (1)	0.001 (1)	0.011 (1)
	C102	0.055 (1)	0.065 (2)	0.073 (2)	−0.016 (1)	−0.008 (1)	0.019 (1)
	C103	0.066 (2)	0.044 (1)	0.074 (2)	−0.009 (1)	−0.028 (1)	0.009 (1)
	C104	0.070 (2)	0.049 (1)	0.052 (1)	0.005 (1)	−0.011 (1)	−0.004 (1)
	C105	0.046 (1)	0.045 (1)	0.054 (1)	0.000 (1)	−0.002 (1)	0.002 (1)
	C200	0.048 (1)	0.045 (1)	0.044 (1)	−0.003 (1)	0.006 (1)	0.005 (1)
	C201	0.057 (2)	0.053 (1)	0.055 (1)	0.003 (1)	0.006 (1)	0.009 (1)
	C202	0.093 (2)	0.049 (1)	0.059 (1)	0.014 (1)	0.027 (1)	0.023 (1)
	C203	0.088 (2)	0.043 (1)	0.081 (2)	0.002 (1)	0.041 (1)	0.002 (1)
	C204	0.065 (2)	0.066 (2)	0.090 (2)	−0.010 (2)	0.020 (2)	−0.018 (1)
	C205	0.057 (1)	0.062 (2)	0.059 (2)	−0.005 (1)	0.004 (1)	−0.008 (1)
	B	0.037 (1)	0.045 (2)	0.040 (2)	0	0	0.001 (2)

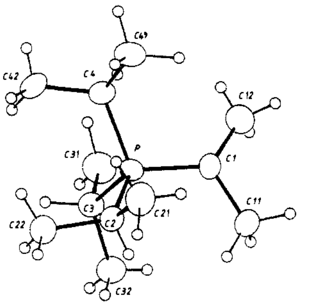


Figure 5. View of **5** perpendicular to the C1–P–C4 plane (ORTEP, thermal ellipsoids 50%, H atoms with arbitrary radii).

certainly be ruled out, it appears likely that the more severe sterical crowding of the ylide molecule **2** which originates from the shortening of one P–C bond (formally to P═C) is relieved by a partial equalization of the bond pair P–C1/P–C4, with the other pair P–C2/P–C3 left largely unchanged.

Turning back to Figure 3, this argument implies that the alleged mirror symmetry with the mirror plane passing through C1, P, and C3 is violated by the different bond lengths P–C2 and P–C4. It is, however, justified by very similar bond angles C1═P—C2 = 107.7 (2) and C1═P—C4 = 108.5 (2)°, as compared to C1═P—C3 = 117.5 (2)°. The increase of the C═P—C angle in ylides well beyond the tetrahedral value as found for C1═P—C3 is a common phenomenon which is borne out by theoretical calculations including studies on the ab initio level with hydrogen substituents attached to phosphorus: $H_3P{=}CR_2$.[10]

Table IV. Selected Interatomic Distances (Å) and Angles (deg) in the Ylide *i*-$Pr_3P{=}CMe_2$, **2** (See Figure 3 for Numbering Scheme Adopted)

P–C1	1.731 (3)	C1–P–C3	117.5 (2)
P–C2	1.842 (3)	C2–P–C4	114.9 (2)
P–C3	1.847 (3)	C1–P–C2	107.7 (2)
P–C4	1.813 (3)	C1–P–C4	108.5 (2)
		C2–P–C3	103.9 (2)
		C3–P–C4	104.5 (2)
C1–C11	1.506 (5)	C11–C1–C12	114.0 (3)
C1–C12	1.492 (5)	P–C1–C11	119.8 (2)
C2–C21	1.504 (5)	P–C1–C12	120.4 (3)
C2–C22	1.542 (5)		
C3–C31	1.513 (5)		
C3–C32	1.530 (4)		
C4–C41	1.521 (5)		
C4–C42	1.517 (5)		

The present structural results show that the cation and anion in **1b** represent two alternative solutions for the accommodation of four $C_s(m)$ or $C_{2v}(mm)$ ligands at a tetrahedral center, i.e., $S_4(\bar{4})$ or $D_2(222)$, respectively. The ylide **2** derived from the cation in **1b** surprisingly shows a good approximation to the highest possible symmetry, namely all-staggered $D_{2d}(\bar{4}2m)$. The origin for this is unknown but is most probably to be sought in the conversion of one isopropyl group into the isopropylide function with concomitant relief of methyl repulsion due to the flattening of the new carbanionic center C1.

Details of the solution of the structure of **2** and a list of atomic coordinates and thermal parameters are presented in the Ex-

Table V. (a) Fractional Atomic Coordinates for Triisopropylphosphonium Isopropylide (**2**). (b) Anisotropic Temperature Factors for **2**

	atom	x	y	z
(a)	P	0.4465 (1)	0.7476 (1)	0.2496 (1)
	C1	0.5518 (5)	0.6247 (4)	0.1848 (3)
	C2	0.3368 (5)	0.8831 (4)	0.1302 (3)
	C3	0.6022 (5)	0.9031 (4)	0.3683 (3)
	C4	0.2845 (5)	0.6045 (4)	0.3234 (3)
	C11	0.6623 (5)	0.7059 (5)	0.0965 (3)
	C12	0.6135 (5)	0.4739 (4)	0.2503 (3)
	C21	0.2017 (5)	0.7826 (5)	0.0220 (3)
	C22	0.2465 (5)	1.0090 (4)	0.1750 (3)
	C31	0.6975 (5)	0.8129 (5)	0.4783 (3)
	C32	0.7494 (5)	1.0342 (4)	0.3197 (3)
	C41	0.1426 (5)	0.4601 (4)	0.2434 (3)
	C42	0.1944 (5)	0.6882 (5)	0.3983 (3)

	atom	$U(11)$	$U(22)$	$U(33)$	$U(23)$	$U(13)$	$U(12)$
(b)	P	0.0295 (5)	0.0226 (4)	0.0249 (4)	−0.0006 (3)	0.0063 (3)	0.0029 (3)
	C1	0.0506 (23)	0.0337 (20)	0.0461 (21)	0.0087 (16)	0.0284 (18)	0.0201 (17)
	C2	0.0309 (19)	0.0341 (19)	0.0350 (19)	0.0029 (15)	0.0116 (16)	0.0111 (16)
	C3	0.0285 (19)	0.0315 (18)	0.0303 (18)	−0.0022 (13)	0.0062 (15)	0.0034 (15)
	C4	0.0327 (19)	0.0308 (19)	0.0373 (20)	0.0003 (15)	0.0132 (16)	0.0009 (16)
	C11	0.0433 (22)	0.0405 (21)	0.0545 (24)	−0.0003 (17)	0.0267 (18)	0.0099 (17)
	C12	0.0364 (21)	0.0404 (22)	0.0594 (25)	0.0046 (18)	0.0147 (18)	0.0140 (17)
	C21	0.0422 (22)	0.0559 (24)	0.0361 (21)	−0.0024 (17)	0.0047 (17)	0.0163 (19)
	C22	0.0402 (21)	0.0418 (21)	0.0487 (22)	0.0081 (17)	0.0159 (17)	0.0204 (17)
	C31	0.0396 (21)	0.0482 (23)	0.0403 (21)	−0.0022 (17)	−0.0018 (17)	0.0069 (18)
	C32	0.0335 (20)	0.0377 (21)	0.0458 (21)	−0.0089 (16)	0.0098 (17)	−0.0038 (16)
	C41	0.0317 (20)	0.0341 (20)	0.0575 (24)	−0.0024 (17)	0.0120 (17)	−0.0049 (16)
	C42	0.0454 (22)	0.0438 (21)	0.0497 (23)	0.0038 (17)	0.0299 (18)	0.0060 (17)

perimental Section and in Table V, respectively.

Experimental Section

The experiments were carried out under dry, purified nitrogen. Solvents and glassware were dried and saturated or filled with nitrogen, respectively.

Tetraisopropylphosphonium iodide (1a) and triisopropylphosphonium isopropylide (2) were prepared as described in ref 8.

Tetraisopropylphosphonium Tetraphenylborate (1b). A sample of 0.45 g (1.36 mmol) of **1a** was dissolved in 4 mL of methanol and heated to 52 °C, before 0.53 g (1.56 mmol) of sodium tetraphenylborate, dissolved in 2 mL of methanol, was added dropwise. A precipitate of **1b** formed immediately, which was separated, washed with 1.5 mL of warm methanol, and dried under vacuum. The product was recrystallized from acetone; colorless needles; yield (crude product) 0.71 g (100%); mp > 210 °C. Anal. Calcd for $C_{36}H_{48}BP$ (522.57): C, 82.75; H, 9.26. Found: C, 82.22; H, 9.22.

X-ray Structure Determinations. Tetraisopropylphosphonium Tetraphenylborate, 1b. A suitable single crystal of **1b** was grown from acetone and sealed under an argon atmosphere into a glass capillary. Precession photographs indicated an orthorhombic unit cell.

The space group $P2_12_12$ was unequivocally determined by the systematic absences and verified by the successful refinement. Reduced cell calculations did not indicate higher symmetry (TRACER[23]). Pertinent crystal data as well as a summary of intensity data collection and structure refinement are given in Table I. The crystal quality was checked by ω scans of several strong, axial reflections. The orientation matrix for the intensity data collection was obtained from the setting angles of 25 centered reflections. After data collection, accurate cell dimensions and their esd's were obtained by a least-squares fit to the Bragg angles of 25 strong high-angle reflections of various parts of reciprocal space accurately centered on an Enraf Nonius CAD 4 automated four-circle diffractometer. The integrated intensities were collected by using graphite-monochromated Mo Kα radiation and $\omega - 2\vartheta$ scans. A variable-scan–variable-speed technique was used. The final scan speed (1–10°/min) was determined by the standard deviation to intensity ratio of a preliminary 10°/min scan. The ω scan width was determined as a function of ϑ to correct for the separation of the Kα doublet; the scan width was calculated as $(0.5 + 0.35 \tan \vartheta)$. The horizontal detector aperture was given by $(3.0 + 0.5 \tan \vartheta)$. Moving-crystal–moving-counter background scans were made by scanning a quarter of the peak width before the start and also after the end of each peak scan. The time spent measuring backgrounds was half that taken to measure the peak. Three monitor reflections served as a check on the centering and stability of the crystal and diffractometer system. They were separated every 4000 s for the intensity check and every 250 reflections for the centering check. As they indicated only a loss of 0.5% in intensity during data collection, a correction for decay was not applied. The intensity of a reflection and its standard deviation were calculated as $I = k[C - 2(\mathrm{BGL} + \mathrm{BGR})]$ and $\sigma(I) = k[C + 4(\mathrm{BGL} + \mathrm{BGR})]^{1/2}$, where C is the peak intensity, BGL and BGR are the left and right background intensities, and k is a constant that depends on the scanning speed. Intensities were corrected for Lorentz and polarization effects ($F_o = (I/Lp)^{1/2}$) but not for those of absorption. Each structure factor amplitude was assigned a standard deviation $\sigma(F_o) = \sigma(I)/2LpF_o$. Only statistically significant ($F_o \geq 4.0\sigma(F_o)$) structure factors were used for all subsequent calculations.

The structure was solved by direct methods (MULTAN 82[24]) and completed by difference Fourier syntheses. After refinement of all non-hydrogen atoms with anisotropic thermal parameters, five hydrogen atoms could be located in a difference Fourier map. All others were calculated at idealized geometrical positions. Thereby found hydrogen atoms served

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982 *J. Am. Chem. Soc.* **1986**, *108*, 982–989

to determine the conformations of all four methyl groups. In the final refinement cycles, hydrogen atoms were included as fixed atom contributions (U_{iso} = 0.05 Å^2), while all other atoms were allowed anisotropic thermal motion. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = [\sigma^2(I) + (pF_o^2)^2]/Lp^2$. p was set to 0.07 to give a "flat" analysis of variance. Refinement of the inverse structure did not yield different results. Neutral, isolated atom scattering factors for all non-hydrogen atoms were those of Cromer and Waber.[25] Scattering factors of the H atoms, based on a bonded spherical atom model, were those of Stewart et al.[26] Corrections for anomalous scattering were applied to all atoms.[27] All calculations were carried out on a PDP 11 using SDP-PLUS.[28]

Triisopropylphosphonium Isopropylide, 2. Colorless single crystals were grown from pentane and sealed under an atmosphere of argon at dry ice temperature into a glass capillary. According to diffractometer measurements (Syntex P2_1), it crystallizes in the triclinic space group $P\bar{1}$. Reduced cell calculations[23] did not reveal any higher symmetry nor did axial photographs. Pertinent crystal data as well as a summary of the intensity data collection and refinement procedure are given in Table I. The integrated intensities of the reflections were measured on a computer-controlled four-circle diffractometer (Syntex P2_1), using graphite-monochromated Mo Kα radiation. A multispeed moving-crystal–stationary-counter technique was used where the peak height at the calculated peak position served to determine the final scan speed. A monitor reflection, examined after every 50 reflections, indicated only a random intensity fluctuation. All other details of the data collection followed closely those described for **1b**.

The structure was solved by direct methods which gave all non-H atom positions (MULTAN 80). After refinement of these atoms (anisotropic thermal parameters), all hydrogen atoms could be located in difference Fourier maps. The methine hydrogen atoms (at C2, C3, and C4) were subsequently refined with isotropic thermal parameters, while the methyl groups were treated as rigid bodies, allowing for rotation around the C–CH$_3$ bonds (U_{iso} = 0.06 Å^2 as fixed thermal parameter for the H atoms). The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. "Unobserved" reflections ($F_o < 4.0\sigma(F_o)$) were omitted in all calculations. Programs used were SHELX 76[29] for refinement, XANADU[30] for geometrical calculations, and ORTEP[31] for the molecular plots. All calculations were done on the departmental VAX 780.

Tetraisopropylphosphonium Iodide, 1a. A data set for **1a** was collected as described for **1b** (above, Table I). The tetragonal symmetry of the diffraction pattern (Laue symmetry $4/m$) and the systematic absences ($hkl = 2n + 1$) indicated $I4$ (no. 79), $I\bar{4}$ (no. 82), and $I4/m$ (no. 87) as possible space groups. For $Z = 2$, only $I\bar{4}$ has special positions with site symmetry possible for an ordered (i-Pr)$_4$P$^+$ cation. With I and P atoms at 0, 0, 0 and 0, 0, 0.5, respectively, R values between 15% and 20% were achieved in $I\bar{4}$. Anisotropic refinement indicated severe displacement of these atoms along the c axis. These special positions do not give sufficient phase information for the structure factor amplitudes, and thus difference Fourier maps did not yield plausible C atom positions. Therefore, the structure solution was not persued further.

Acknowledgment. Our work was generously supported by Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Hoechst AG and Ciba AG. C.M.F. Frazão is grateful to DAAD, Bonn, for a research fellowship.

Registry No. 1a, 92209-07-9; **1b**, 92209-04-6; **2**, 99829-77-3.

Supplementary Material Available: Additional crystal structure data, tables with H atom parameters, and observed and calculated structure factor amplitudes (38 pages). Ordering information is given on any current masthead page.

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Aluminum Alkoxide Chemistry Revisited: Synthesis, Structures, and Characterization of Several Aluminum Alkoxide and Siloxide Complexes

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Abstract: Several [Al(OR)$_2$(β-diketonate)]$_n$ (OR = alkoxide or siloxide) and [Al(OR)(β-diketonate)$_2$]$_2$ complexes have been prepared and characterized in solution and in the solid state. The unique structures of [Al(OR)$_2$(acac)]$_n$ compounds (acac = acetylacetone; n = 1 for R = SiPh$_3$; n = 2 for R = SiMe$_3$, i-Pr, and t-Bu; n = 3 for R = i-Pr) contain tetrahedral and octahedral aluminum sites, and n is dependent on the size of the alkoxide or siloxide ligand. The [Al(OR)(β-diketonate)$_2$]$_2$ complexes (for R = i-Pr, β-diketone = acetylacetone, 3,5-heptanedione, and ethyl acetoacetate; for R = Me, β-diketone = ethyl acetoacetate) are dimers containing two octahedral aluminum centers bridged by alkoxide groups. These compounds are thermally unstable in solution and decompose via ligand disproportionation to Al (β-diketonate)$_3$ and [Al(OR)$_2$(β-diketonate)]$_n$. The disproportionation of [Al(O-i-Pr)(acac)$_2$]$_2$ follows first-order kinetics with a highly positive entropy factor. Dynamic ^{1}H NMR spectra of [Al(O-i-Pr)(acac)$_2$]$_2$ show isomerism between meso and d,l isomers and restricted rotation of the bridging isopropoxide groups at low temperatures.

We describe in this report the synthesis and characterization of several Al alkoxide and siloxide β-diketonate complexes. Included in the study are Al compounds of the general formula [Al(OR)$_2$(acac)]$_n$ (acac = acetylacetone; n = 1 for R = SiPh$_3$; n = 2 for R = SiMe$_3$, i-Pr, and t-Bu; n = 3 for R = i-Pr) and [Al(OR)(β-diketonate)$_2$]$_2$ (for R = i-Pr, β-diketone = acetylacetone, 3,5-heptanedione, and ethyl acetoacetate; for R = Me, β-diketone = ethyl acetoacetate). These compounds have unprecedented structures and reactivity and pose some interesting considerations as to their activity as catalysts and ceramic precursors.

Considerable research has been devoted to understanding the structures of aluminum alkoxide and siloxide complexes.[1] The

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(1) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. "Metal Alkoxides"; Academic Press: New York, 1978.

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