Chart I

1   2   3 L_1= Ph, L_2= Et   4 L_1= Me, L_2= OCH(CF₃)₂

3' L_1= Et, L_2= Ph   4' L_1= OCH(CF₃)₂, L_2= Me

5   5'   6   7 L= Me, L'= Ph

or L= Ph, L'= Me

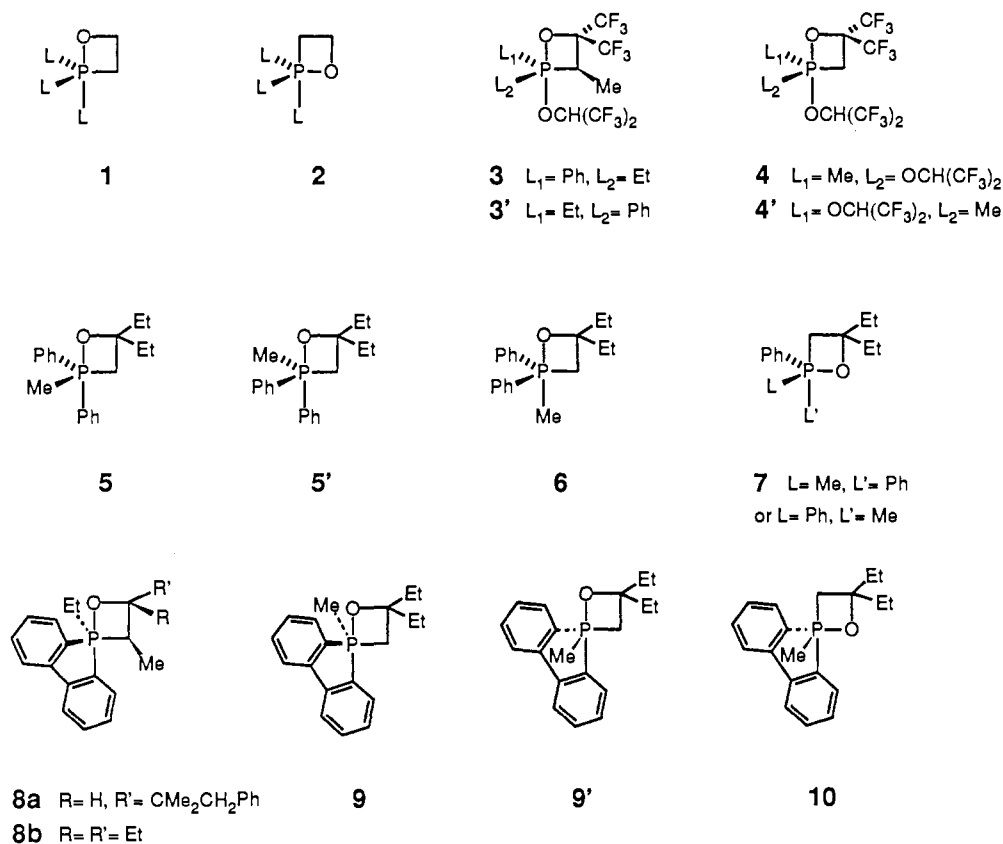8a R= H, R'= CMe₂CH₂Ph   9   9'   10

8b R= R'= Et

Even though $\Delta G^{\ddagger}_{DEC}$ is of much higher energy than $\Delta G^{\ddagger}_{PSDRTN}$, there can still be an *apparent* correlation between slow decomposition rates and slow pseudorotation in certain oxaphosphetanes such as 3 and 4 compared to 5. Consider the relevant transition-state geometries; TS_{PSDRTN} lies between 1 and 2, and will increasingly resemble 2 as the stability of 2 vs 1 decreases (Hammond postulate). Since 2 has equatorial oxygen, the partly rehybridized P–C₃ bond in TS_{PSDRTN} will be longer than in 1. TS_{DEC} should also have an elongated P–C₃ bond because advanced P–C vs C–O bond breaking is predicted according to bond strength comparisons as well as calculations.[1] Both TS_{DEC} and TS_{PSDRTN} in 3 or 4 will therefore be destabilized by the electronegative CF₃ groups, substituents that favor trigonal-bipyramidal structures, apical oxygen geometries, and shorter (equatorial) P–C₃ bonds.[12] The result will be a decrease in k_{DEC} and a *coincidental* decrease in k_{PSDRTN}. In more typical Wittig intermediates, the geometry of TS_{DEC} leading to alkene could be increasingly different from the geometry of 2 or of TS_{PSDRTN}. However, the geometric options are severely restricted for any cyclic 4-membered structure that contains phosphorus, and TS_{DEC} will have certain geometric features in common with 2 regardless of mechanistic details.

The conclusion that both TS_{DEC} and TS_{PSDRTN} have an elongated P–C₃ bond does not mean that 2 is a required intermediate[13] or that any specific pseudorotamer is necessary before decomposition can occur. A preequilibrium of 1 with 2 affects decomposition rates only if (1) TS_{PSDRTN} is greater than or comparable to TS_{DEC} in free energy, or (2) if 2 is more stable than 1. Otherwise, the relative populations of pseudorotamers or the path to the transition state can have no kinetic significance (Curtin–Hammett principle).[14] Advanced P–C₃ bond breaking in the decomposition step is likely in any event, and this interpretation

would apply to a diradical cleavage as well as to an asynchronous cycloreversion. We prefer the latter description for the decomposition of typical Wittig intermediates to alkenes and phosphine oxide pending further evidence.

A Novel Example of a Di-μ-chloro-Stabilized Octahedral Coordination of Aluminum by Cyclam. Synthesis and Molecular Structure of [(CH₃)₂AlCl]₂[Al·C₁₀H₂₀N₄][Al(CH₃)₂]

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For some time now this laboratory has had an interest in the organoaluminum chemistry of multidentate amines. Interactions of organoaluminum species with multidentate amines containing N–H fragments have proven to be quite interesting in that such systems, characteristically involving Al–R/N–H bond cleavage, result in novel organoaluminum products possessing extensive aluminum–nitrogen networks. We have recently reported several such unusual organoaluminum compounds.[1–6] To assess the

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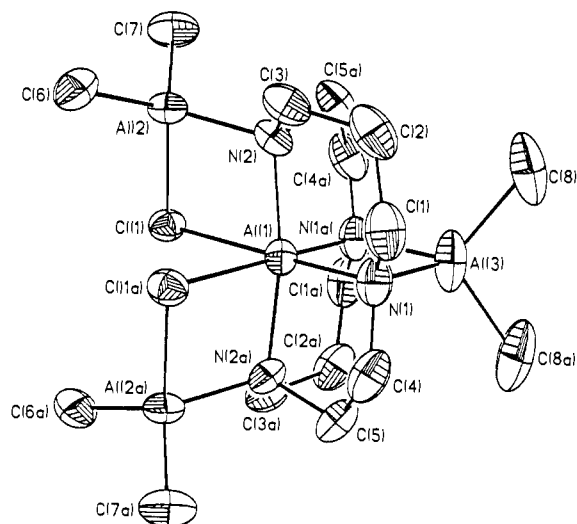
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Figure 1. A view of the $[(CH_3)_2AlCl]_2[Al\cdot C_{10}H_{20}N_4][Al(CH_3)_2]$ molecule showing the atom-labeling scheme. Thermal ellipsoids show 35% probability levels; hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg): Al(1)–N(1), 1.952 (3); Al(1)–N(2), 1.981 (3); Al(1)–Cl(1), 2.509 (2); Al(2)–Cl(1), 2.258 (2); Al(3)–C(8), 1.986 (6); Al(2)–C(6), 1.942 (4); Al(2)–C(7), 1.965 (4); N(2)–Al(1)–N(2a), 170.0 (2); Cl(1)–Al(1)–N(1), 177.0 (1); Cl(1)–Al(1)–N(1a), 93.6 (1); Cl(1)–Al(1)–N(2), 81.1 (1).

possible effects of transition-metal salts on these Al–N systems, $ZrCl_4$ was allowed to interact with an organoaluminum-macrocyclic amine system. Herein we report the synthesis[7] and molecular structure of $[(CH_3)_2AlCl]_2[Al\cdot C_{10}H_{20}N_4][Al(CH_3)_2]$, isolated from reaction of 1,4,8,11-tetraazacyclotetradecane, cyclam ($C_{10}H_{24}N_4$), with trimethylaluminum and $ZrCl_4$. Particularly noteworthy is the fact that the title compound contains a six-coordinate aluminum atom in an octahedral environment. Additionally, the macrocycle in $[(CH_3)_2AlCl]_2[Al\cdot C_{10}H_{20}N_4][Al(CH_3)_2]$ has assumed an interesting folded conformation. The title compound represents the first report of cyclam assuming the folded conformation where a group 13 (IIIA) metal is concerned. The X-ray crystal structure of this neutral organoaluminum compound is shown in Figure 1.
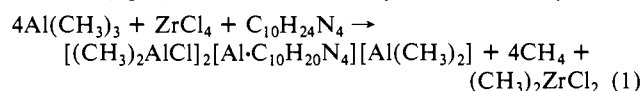
X-ray intensity data were collected on a Nicolet R3m/V diffractometer using an $\omega/2\theta$ scan technique with Mo Kα radiation (λ = 0.71073 Å) at 21 °C. The title compound crystallizes in the monoclinic space group $C2/c$ with unit cell parameters a = 17.643 (7) Å, b = 11.220 (6) Å, c = 13.069 (5) Å, β = 104.56 (3)°, V = 2504 (2)°, and D_{calcd} = 1.23 g cm^{-3} for Z = 4. The structure was solved by direct methods and refined, based on 1430 observed reflections ($I > 3\sigma(I)$), using SHELXTL PLUS.[8] Least-squares refinement converged at R = 0.0392 (R_w 0.0566). Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were located by standard difference Fourier techniques; methylene hydrogen atoms were refined by using isotropic thermal parameters while methyl hydrogen atoms were included in the structure factor calculation at idealized positions (d_{C-H} = 0.96 Å).

The organoaluminum chemistry of monodentate primary and secondary amines was first examined extensively in the seminal work of Smith.[9-17] Recent studies in our laboratory concerning the organoaluminum chemistry of macrocyclic and multidentate open-chain amines have revealed a rich and varied chemistry particularly with regard to coordination environments of the associated aluminum atoms. The role of transition-metal salts in these systems represented an interesting extension of this work. Thus we endeavored to examine the effect of $ZrCl_4$ on the well-studied organoaluminum–cyclam system.[2,6]

This unusual $[(CH_3)_2AlCl]_2[Al\cdot C_{10}H_{20}N_4][Al(CH_3)_2]$ complex results from a unique reaction involving the cleavage of N–H and Al–R bonds (resulting in methane elimination) and the chlorination of aluminum by $ZrCl_4$. While it is evident that $ZrCl_4$ played a profound role in the formation of the title compound, no zirconium species were isolated. Alkylzirconium derivatives such as $(CH_3)_4Zr$ are inherently unstable and reportedly decompose, with blackening, above −15 °C.[18] Notably, a considerable amount of black-brown residue was observed in the reaction vessel. As demanded by mass balance, the balanced equation of the reaction (eq 1) includes the dimethylzirconium complex (C-

$$4Al(CH_3)_3 + ZrCl_4 + C_{10}H_{24}N_4 \rightarrow$$
$$[(CH_3)_2AlCl]_2[Al\cdot C_{10}H_{20}N_4][Al(CH_3)_2] + 4CH_4 +$$
$$(CH_3)_2ZrCl_2 \quad (1)$$

H$_3$)$_2$ZrCl$_2$. It is important to note that $(CH_3)_2ZrCl_2$ is quite unstable. While earlier attempts at preparing $(CH_3)_2ZrCl_2$ from reaction of ZrX_4 and ZnR_4 (X = Cl, Br; R = CH_3, C_2H_5) failed, the workers were able to isolate the bipyridine adduct of $(CH_3)_2ZrCl_2$.[19]

Several points are worthy of note regarding structure and bonding in the novel $[(CH_3)_2AlCl]_2[Al\cdot C_{10}H_{20}N_4][Al(CH_3)_2]$ complex. The molecule resides about a twofold axis coincident with Al(1) and Al(3) (Figure 1). Particularly significant is the fact that the central aluminum atom, Al(1), is six-coordinate, residing in an octahedral environment bonding to the four nitrogen atoms of the amine in addition to two chlorine atoms that are bridging two dimethylaluminum units. The central aluminum atom is coplanar with N(1), N(1a), Cl(1), and Cl(1a), while the two remaining nitrogen atoms of the amine, N(2) and N(2a), are in axial positions relative to this N_2AlCl_2 plane. The N(2)–Al(1)–N(2a) bond angle is 170.0 (2)°, while the Cl(1)–Al(1–)–N(1) bond angle is 177.0 (1)°.

The macrocycle in $[(CH_3)_2AlCl]_2Al\cdot C_{10}H_{20}N_4][Al(CH_3)_2]$ has experienced substantial distortion. Indeed, the four nitrogen atoms of the macrocycle have been forced to assume a folded conformation. This folded conformation has been suggested as a means by which tetraazamacrocycles interact with metal ions that are too large for the central macrocyclic cavity.[20-25] The independent

(7) Inside the drybox a reaction vessel was charged with cyclam (4.98 mmol), $ZrCl_4$ (4.98 mmol), and chlorobenzene (15 mL). The mixture was stirred for 3 h at room temperature; no reaction was apparent. Trimethylaluminum (10 mmol) was slowly added via syringe. The reaction vessel containing the milky white mixture was removed from the drybox and heated in an oil bath (120 °C for 1 h) during which time reaction was quite apparent. The reaction vessel was vented frequently to release CH_4, which was eliminated during the course of the reaction. Upon cooling, a clear solution resulted accompanied by a considerable amount of dark brown precipitate. The solution was filtered via cannula to a 100-mL Schlenk flask. Reduction of solvent and subsequent cooling of the flask resulted in the formation of slightly yellow, air-sensitive X-ray-quality crystals in approximately 30% yield. Melting point: 215 °C (dec). ^1H NMR (CDCl$_3$): δ −0.687 (s, 6 H, Al-(CH$_3$)$_2$); −0.561 (s, 6 H, Al(CH$_3$)$_2$Cl); −0.531 (s, 6 H, Al(CH$_3$)$_2$Cl); 1.45–3.52 (m, 20 H, (N(CH$_2$)$_2$N(CH$_2$)$_3$)$_2$).

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Al–N distances are 1.952 (3) and 1.981 (3) Å for Al(1)–N(1) and Al(1)–N(2), respectively. The Al(1)–Cl(1) and Al(2)–Cl(1) bond distances of 2.509 (2) and 2.258 (2) Å, respectively, are longer than Al–Cl distances reported in two previously reported AlCl$_2$–crown ether complexes containing octahedral aluminum atoms: [AlCl$_2$][12-crown-4]$^+$ (2.202 (5) Å) and [AlCl$_2$][18-crown-6]$^+$ (2.148 (3) Å).[26] Indeed, the Al–Cl distances in the title compound are longer than the Al–Cl distances reported for the seven-coordinate aluminum atom in [AlCl$_2$][benzo-15-crown-5]$^+$ (2.202 (5) and 2.197 (7) Å).[27]

The isolation of the unusual organoaluminum compound has stimulated our interest in cyclam–zirconium systems. In future contributions we will continue to explore the role of transition-metal salts on the organoaluminum chemistry of macrocyclic amines.

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Ultrasound-Promoted Diels–Alder Reactions: Syntheses of Tanshinone IIA, Nortanshinone, and (±)-Tanshindiol B

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The *o*-quinone abietanoid pigments of the Chinese sage, *Salvia miltiorrhiza* Bunge, are responsible for the broad spectrum of biological activity of the Chinese traditional medicine Dan Shen,[1] prepared from the roots of this species.[2] Many of the active compounds, including secondary metabolites present in only small quantities,[3] can conceivably be prepared by simple Diels–Alder

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cycloadditions of *o*-quinone **1** with appropriate dienes. Previously
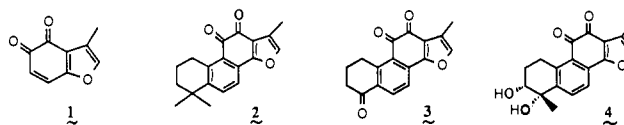
we reported the preparation of **1** and examined its dienophilicity.[4] While **1** was quite reactive with active dienes such as cyclopentadiene, its thermal instability rendered it of limited applicability with more interesting vinylcyclohexene derivatives unless high pressures (11 kbar) were employed. We now report that the cycloadditions can be promoted by ultrasound in the absence of solvent, and we have used this method to synthesize tanshinone IIA (**2**), nortanshinone (**3**), and (±)-tanshindiol B (**4**), active constituents of *S. miltiorrhiza*. This report represents the first example of an ultrasound-promoted Diels–Alder cycloaddition.

The results of the cycloadditions are presented in Table I. The dienes were prepared by the palladium-catalyzed vinyl coupling of tri-*n*-butylvinylstannane with enol triflates as described by Stille (Scheme I).[5] The cycloadditions were best performed in the absence of solvent,[6] though the insolubility of **1** in isoprene (**7**) as well as the volatility of **7** (bp 36 °C) required the use of a solvent (methanol) for this reaction. Increasing amounts of solvent led to decreased yields of cycloadducts (also entry 5, Table I). In a control experiment, heating vinylcyclohexene **5** and *o*-quinone **1** to 45 °C for 2 h did not yield cycloadducts; longer heating (16 h) led only to decomposition of **1**. The cycloadducts were obtained as a mixture of the tetrahydro and dihydro forms. The tetrahydro cycloadducts oxidized to the dihydro compounds upon standing or upon chromatography with silica gel. Stirring the product mixture in oxygen in the presence of silica gel or refluxing with DDQ in benzene yielded the fully aromatized cycloadducts.

The results in Table I indicate that ultrasound is not only effective in promoting the cycloadditions but also improves the regioselectivity. For example, the cycloaddition of diene **10** with **1** in refluxing benzene gave only a 15% yield of cycloadducts in a ratio of 1:1 while sonication of a neat mixture of **10** and **1** gave a 76% yield of cycloadducts with the desired regioisomer, **20** favored 5:1. Deprotection of **20** (Dowex-50, H$^+$ form, 50% aqueous THF, 70 °C, 12 h) yielded **4**. Cis diol **4** proved to be identical with tanshindiol B, originally assigned the trans structure. Epimerization of the cis diol unit to the trans during deprotection of the acetonide **20** was ruled out by reprotection of synthetic **4** to the identical acetonide **20**. An NOE between the methyl at C-4 and H-3 in the re-formed **20** confirmed the cis stereochemistry of the diol unit. Thus tanshindiol C (**22**), also isolated from *S. miltiorrhiza*, must have the trans diol unit, not the cis as originally assigned.[7]

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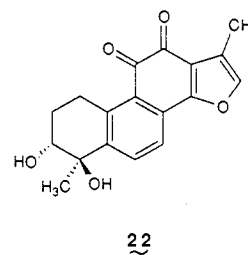
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(6) In a typical procedure, *o*-quinone **1** (100 mg, 0.617 mmol) was placed in a conical reaction vial with the diene (3–5 equiv) and the mixture placed in an ultrasonic cleaner (50/60 kHz, 125 W) for 1–2 h. The temperature was maintained below 45 °C.