2, 3 shows an intense band (538 nm; ϵ 62 000) in the visible absorption spectrum and two strong emission bands (uncorrected) at 563 and 825 nm.

Generally, the few known examples of thallium(I) (or lead(II)) transition-metal bonding are considered to involve primarily ionic interactions.[9] However, this is clearly not the case in **2** and **3**. We view the primary thallium–iridium bonding as involving the interaction of the filled $5d_z{}^2$ orbitals and empty $6p_z$ on iridium with the filled $6s$ and empty $6p_y$ and $6p_z$ orbitals on thallium (local Tl x axis perpendicular to the Ir–Tl–Ir plane, z axis bisects the Ir–Tl–Ir angle). A simple group theory treatment using these orbitals leads to the diagram shown in Figure 2.[10] Mixing between levels will stabilize the filled a_1, b_2, and a_1 orbitals relative to their empty counterparts, thereby imparting stability to the Ir–Tl–Ir unit. It is proposed that the lowest energy absorption bands leading to luminescence in **2** and **3** result from an a_1 to a b_2 or a_1 transition localized within the Ir–Tl–Ir moiety.

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and data collection parameters for **2** (9 pages). Ordering information is given on any current masthead page.

(9) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980, p 350. (b) Tl[Co(CO)$_4$]: Tl···Co (3.551 Å) Schussler, D. P.; Robinson, W. R.; Edyell, W. F. *Inorg. Chem.* **1974,** *13*, 153. (c) Tl[Au(CN)$_2$]: Tl···Au (3.45 Å) Blom, N.; Ludi, A.; Bürgi, H.-B.; Tichy, K. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984,** *C40*, 1967. (d) Pt(PPh$_3$)$_2$(C$_6$H$_5$)Pb(C$_6$H$_5$)$_3$: Pt–Pb (2.698 Å) Crocinai, B.; Nicolini, M.; Clemeute, D. A.; Bandoli, G. *J. Organomet. Chem.* **1973,** *49*, 249.

(10) The relative positionings of the orbital energies are of necessity somewhat arbitrary but are placed so as to coincide with the theoretical values reported from Dirac–Fock SCF calculations for the free atoms (Desclaux, J. P. *At. Data Nucl. Data Tables* **1973,** *12*, 311).

Figure 2. Top: perspective drawing of [Ir$_2$Tl(CO)$_2$Cl$_2$(μ-dpma)$_2$]$^+$ showing 50% thermal elipsoids for heavy atoms and uniform arbitrarily sized circles for carbon and oxygen atoms. Selected interatomic distances (Å): Ir(1)–Tl, 2.958 (1); Ir(2)–Tl, 2.979 (1); Ir(1)–P(1), 2.323 (4); Ir(1)–P(3), 2.332 (4); Ir(1)–Cl (1), 2.369 (4); Ir(1)–C(65), 1.79 (1); Ir(2)–P(2), 2.328 (4); Ir(2)–P(4), 2.339 (4); Ir(2)–Cl(2), 2.358 (4); Ir(2)–C(66), 1.83 (2); Tl···As(1), 3.295 (3); Tl···As(2), 3.308 (3). Selected interatomic angles (deg): Ir(1)–Tl–Ir(2), 139.4 (1); P(1)–Ir(1)–P(3), 170.0 (1); Cl(1)–Ir–C(65), 170.9 (5); P(1)–Ir(1)–Cl(1), 86.4 (1); P(1)–Ir(1)–C(65), 92.7 (5); P(3)–Ir(1)–Cl(1), 89.0 (1); P(3)–Ir(1)–C(65), 90.4 (5); P(2)–Ir(2)–P(4), 168.9 (1); Cl(2)–Ir(2)–C(66), 173.0 (5); P(2)–Ir(2)–Cl(2), 87.7 (1); P(2)–Ir(2)–C(66), 92.3 (5); P-(4)–Ir(2)–Cl(2), 87.7 (1); P(4)–Ir(2)–C(66), 91.1(5). Bottom: qualitative molecular orbital diagram for the Ir$_2$Tl unit.

valently bound to the cation. It rests in front of the thallium ion and in the Ir$_2$Tl plane, but the shortest Tl···O separation is 2.798 Å, much longer than the Tl–O separation of 2.46 Å found in gaseous TlNO$_3$[7] and of 2.101 Å found in gaseous Tl$_2$O.[8]

Lead(II), which is isoelectronic with thallium(I), also forms a complex with **1**. Addition of lead(II) nitrate in methanol to **1** in dichloromethane produces a pink solution from which [Ir$_2$Pb-(CO)$_2$Cl$_2$(μ-dpma)$_2$](NO$_3$)$_2$, **3**, has been isolated as shocking pink crystals. Its spectroscopic properties (^{31}P NMR 24.4 ppm; infrared, ν(CO), 1978, 1984 cm^{-1}) are similar to those of **2**. Like

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Organosulfones as Chemical Chameleons. A Ring Expansion to α-Methoxy and α-Phenylthio Ketones

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The importance of ring-expansion methods in organic synthesis and the weakness of existing ones is underscored by the large continuing effort to develop new approaches.[1-3] Of prime im-

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Table I. Ring Expansion to α-Phenylthio Ketones

entry	ketones	addn product	yield[a]	temp, °C/time, h	product	overall yield[c]
1			92%	−20/4		79%
2			94%[b]	−78/3		77%
3			92%	−78/1		72%
4			92%	−78/0.33		69%
5			95%[b]	0/1		66%
6			93%	−78/1.5		74%

[a] For isolated pure product unless otherwise stated. [b] Crude yield. [c] Overall yield for isolated pure product from starting ketone. All new compounds have been fully characterized spectroscopically and elemental compositions established by high-resolution mass spectroscopy and/or combustion analysis.

portance to us is the ability to introduce a substituent, particularly a heteroatom substituent,[3] concomitant with the expansion. Our discovery of the sensitivity of sulfones as a leaving group in the presence of Lewis acids[4,5] suggests that such compounds may be useful in ring expansions (eq 1). The development of sulfones
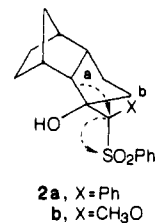

(1)
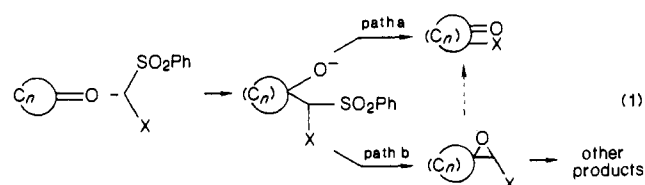
for such purposes has the advantage that the sulfone is such a good acidifying group[6] that the substituent need not be an anion stabilizing group. A common competing process that can thwart the desired ring expansion (eq 1, path a) is formation of epoxides (eq 1, path b)—a process that sometimes intervenes in ring expansions via diazo compounds and poly(phenylthio) compounds and subsequently can lead to undesired products. The low nucleophilicity of a benzenesulfinate anion compared to benzenethiolate, the ready generation of anions adjacent to sulfone even when X is anion destabilizing, and the ability to promote ionization of the sulfone under mild conditions lead us to test the feasibility of eq 1, path a. We wish to report that sulfone-stabilized anions are convenient

reagents for regioselective ring expansions to both α-phenylthio and α-methoxy ketones and that the latter can be accomplished in a simple one-pot operation.

Surprisingly, the lithium derivative of (phenylthio)methyl phenyl sulfone (1),[7] generated with n-butyllithium in THF at −78 °C, adds very poorly to ketones. On the other hand, addition of a solution of excess diethylaluminum chloride in hexane to the mixture of the lithium derivative of 1 and ketone in THF led to smooth anion addition to the carbonyl group as summarized in Table I. The aluminum reagent can be introduced prior to or following the ketone with no noticeable effect.

Rearrangement proceeds smoothly by treating the adduct in methylene chloride at −78 °C with an approximately sixfold excess of diethylaluminum chloride.[8] In some cases, the temperature is raised prior to quenching with aqueous sodium bicarbonate as summarized in Table I. The last column lists the yields for the overall process of ring enlargement from starting ketone. In each case, except for entry 6, migration of that carbon that can best stabilize an electron deficiency at the transition state occurs. A possible explanation for the exception relates to the conformational rigidity imposed upon the five-membered ring by the norbornyl fragment as depicted in 2a. Migration of bond a proceeds through

2a, X=Ph
b, X=CH₃O

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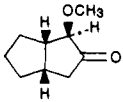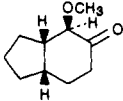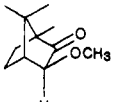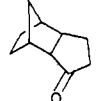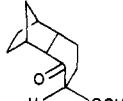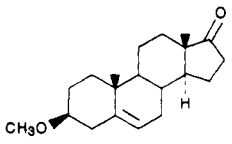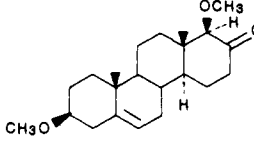
(8) This rearrangement fails in ethereal solvents.

Table II. Ring Expansion to α-Methoxy Ketones

| entry	ketone	temp,[a] °C/time, h	ring expanded product	isolated yield[b]
1[c]		−78/7		68
2[d]		−78/2 −30/1	**6**	76 (85)
3[d]		−50/2		73 (86)
4[d]		−60/5		63%
5[e]		rt/16	**8**	61%

[a] All additions of the [methoxy(phenylsulfonyl)methyl]lithium to the ketone were performed at −78° C. The temp/time recorded here is for the in situ rearrangement step. [b] all yields are for isolated pure product. Yields in parentheses are based upon recovered starting material. [c] Better results were obtained by using diisobutylaluminum chloride for the rearrangement. [d] Diethylaluminum chloride was employed for the rearrangement step. [e] Diisobutylaluminum diisopropylamide was required for the rearrangement.

a boat-type transition state; whereas, migration of bond b proceeds through a half-chair.[9] It should be noted that both five- and six-membered ring ketones participate satisfactorily in contrast to other sulfur-based ring expansions.[3]

A possible advantage of the sulfur leaving group is the extension to introduction of other heteroatoms concomitant with ring expansion. Oxygen is among the most important. We, therefore, examined the use of the methoxymethyl phenyl sulfone (3)[10] for ring expansions. Addition of the lithium derivative, generated by using tert-butyllithium at −78 °C, in DME to ketones such as 4 proceeded in excellent yields in contrast to the addition of the phenylthio derivative. We attribute the success to a lower
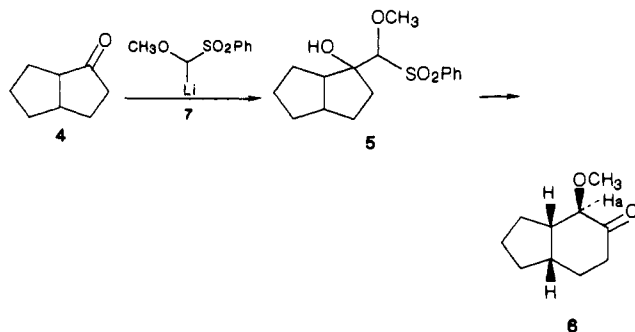
reversibility of the initial addition due to the poorer anion-sta-

bilizing ability of a methoxy group compared to a phenylthio group. Exposure of 5 to aluminum chloride (CHCl₃, 0 °C) gave a 53% yield of the ring-expanded ketone 6. The sensitivity of the initial adduct 5 and the decomposition of the product by aluminum chloride led to in situ treatment of the initial adduct (i.e., the lithium salt of 5) with milder Lewis acids. Indeed, addition of the lithium derivative of sulfone 3 (i.e., 7) to ketone 4 in DME at −78 °C followed by diethylaluminum chloride and workup gave the ring-expanded ketone directly in 76% overall yield from 4. The ability to promote a Lewis acid catalyzed rearrangement in an ethereal solvent like DME attests to the facility of the rearrangement. The product, a single regio- and diastereomer, is assigned as 6 based upon its ¹H NMR spectrum (H$_a$, δ 4.13, dd, J = 6.6, 1 Hz).

This one-pot sequence was employed for all the ring expansions listed in Table II. Some variation of the Lewis acid was required. For example, employment of diisobutylaluminum chloride gave somewhat improved yields in the case of entry 1. Most dramatically, all the aluminum chlorides proved inadequate in the steroid case. Surprisingly, the extremely mild Lewis acid diisobutylaluminum diisopropylamide[11] successfully effected the desired rearrangement in this case.

The regiochemistry followed the trend of the more substituted carbon undergoing preferential migration except for entries 3 and 4. The abnormal behavior of bicyclo[2.2.1]heptyl systems has previously been noted in ring expansions[2c,9] and we have noted the abnormal behavior of the ketone of entry 4 with the phenylthio reagent 1. Both cases are rationalized by the conformational preference for a chair rather than a boat-type transition state for the rearrangement as depicted in 2. For entries 1–4, a single diastereomer resulted whose assignment rests on the NMR data as indicated for 6. In each case, this also appears to correspond to the thermodynamically more stable isomer. For the steroid

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product **8**, only a single isomer also results; its stereochemistry is assigned by analogy.

This approach for ring expansion to α-methoxy ketones proceeds well for four- and five-membered rings. At present, larger rings do not succumb to ring expansion in contrast to the phenylthio reagent **1**. The reason for the difference may relate to the better ability of oxygen vs. sulfur to stabilize a positive charge. The higher stability associated with the presumed intermediate in the oxygen series, i.e., **9**, compared to the sulfur series, i.e., **10**, may provide a smaller driving force for rearrangement.
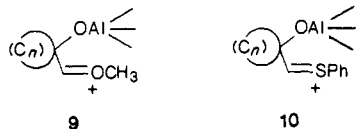
α-Thio- and α-alkoxy sulfones are excellent conjuctive reagents for ring expansion to α-heteroatom-substituted cycloalkanones. In contrast to reagents like diazo compounds, they are more available, simpler and safer to handle, and they offer greater structural flexibility. Analogues of the rearrangements reported herein are not known for the diazo series. The better anion-stabilizing abilities of a sulfone compared to a sulfide also make these reactions more general than the corresponding reactions using thio ethers.[12] The ability of sulfones to be chemical chameleons, i.e., to be nucleophiles in the presence of base and electrophiles in the presence of acid, appears to provide great opportunities for designing new reagents and reactions.

(12) In control experiments, we find that lithiated methoxymethyl phenyl sulfide[13] which we previously employed for ring expansions of lactones cannot be used for ring expansions of cycloalkanones. A ring expansion of a (butylthio)methylenecyclohexanone has been reported: Bosch, M. P.; Camps, F.; Coll, J.; Guerrero, A.; Tatsuoka, T.; Meinwald, J. *J. Org. Chem.* **1986**, *51*, 773.

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Models for Organometallic Molecule-Support Complexes. Synthesis and Properties of Cationic Organoactinides

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Received February 19, 1987

Chemical and ^{13}C CPMAS NMR data[1] suggest that cationic species play a major role in the surface and possibly catalytic chemistry of actinide alkyls (and by inference, of many other organometallics[2]) on electron-deficient metal oxide supports (e.g.,

Figure 1. Molecular structure of the cation portion of Cp$_2$'Th(Me)-(THF)$_2$$^+BPh_4$$^-$ (**7**). Important bond distances (Å) and angles (deg) are Th-C(1) = 2.49 (1), Th-O(1) = 2.531 (9), Th-O(2) = 2.628 (8), Th-C$_{ring}$ = 2.80 (1,2,4,10),[12] C(1)-Th-O(1) = 72.9 (4), C(1)-Th-O(2) = 140.2 (4), and ring centroid–Th–ring centroid = 136.2. Thermal ellipsoids are at the 30% probability level.

γ-Al$_2$O$_3$). Straightforward solution routes to model cationic organoactinide alkyls and complexes free of coordinating[3] bases would be highly desirable, and we report here the first efficient synthetic approach as well as initial observations on the properties of the products. Base-coordinated Cp$_2$Zr(Me)L$^+$ complexes have recently been prepared via a completely different route.[4]

Trialkylammonium tetraphenylborate reagents[5] effect quantitative (by NMR) protonolysis of actinide alkyls in *noncoordinating* solvents to yield cationic tetraphenylborates (eq 1–3). For

$$\text{Cp}'_2\text{ThMe}_2 + \text{R}_3\text{N}^+\text{H BPh}_4^- \xrightarrow[-\text{MeH}]{\text{toluene}}$$

$$\text{Cp}'_2\text{Th(Me)NR}_3^+ \text{ BPh}_4^- \xrightarrow{-\text{NR}_3} \text{Cp}'_2\text{Th(Me)}^+ \text{ BPh}_4^- \quad (1)$$

1a, R = Me, 70% isolated, yield
1b, R = Et   **2**, 90% isolated yield

$$\text{Cp}'_2\text{Th}(o\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)\text{Me} + \text{Et}_3\text{N}^+\text{H BPh}_4^-$$
3

$$\xrightarrow[-\text{NEt}_3]{\text{toluene}} \text{Cp}'_2\text{Th}(o\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)^+\text{BPh}_4^- \quad (2)$$
          4, 88% isolated yield

$$\text{Cp}^*_3\text{ThMe} + \quad \text{Et}_3\text{N}^+\text{H BPh}_4^- \xrightarrow[-\text{NEt}_3]{\text{toluene}}$$
          5a, Cp* = CH$_3$C$_5$H$_4$
          5b, Cp* = Me$_3$SiC$_5$H$_4$
                    Cp$_3^*$Th$^+$BPh$_4^-$ (3)
          6a, Cp* = CH$_3$C$_5$H$_4$, 82% isolated yield
          6b, Cp* = Me$_3$SiC$_5$H$_4$, 70% isolated yield

Me$_3$N, intermediate amine complexes are sometimes isolated (**1a**), while bulkier Et$_3$N forms labile adducts that dissociate upon workup, yielding base-free cationic products. All new compounds

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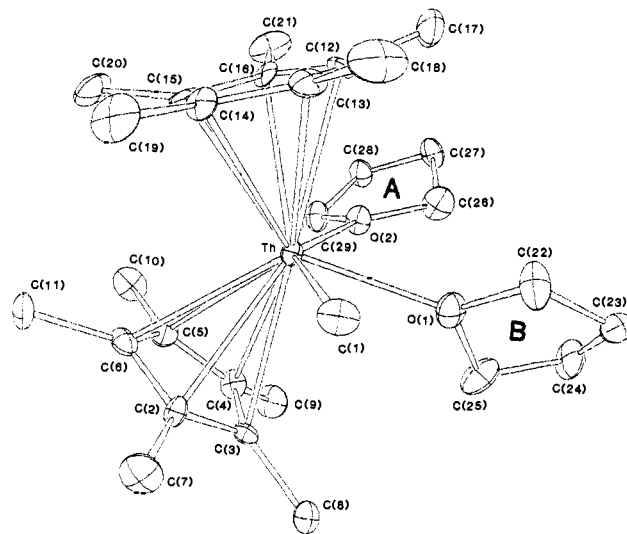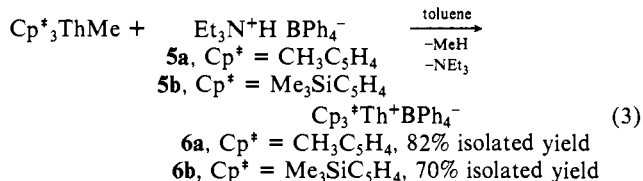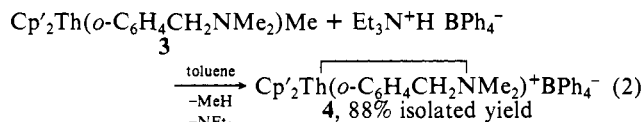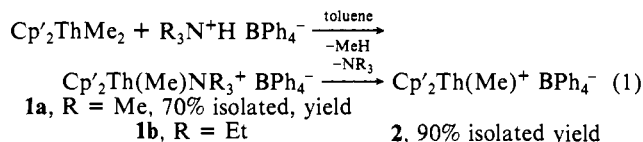
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