

reactions. For  $n\text{-C}_4\text{H}_{10}$  hydrogenolysis over Ir(110)-(1 $\times$ 2), however, both the specific rate (apparent activation energy of  $22 \pm 2$  kcal mol $^{-1}$ ) and the selectivity (to  $\text{C}_2\text{H}_6$ ) are qualitatively different, indicative of the presence of a qualitatively different surface intermediate. Furthermore, by varying the partial pressures of the reactants, we have observed that *whatever* the intermediate from  $n\text{-C}_4\text{H}_{10}$  on Ir(110)-(1 $\times$ 2) is, it is *less dehydrogenated* than either the intermediate from  $n\text{-C}_4\text{H}_{10}$  on Ir(111) or the intermediate from  $\text{C}_3\text{H}_8$  on both surfaces.<sup>20</sup> These observations suggest *strongly* that the occurrence of this particular intermediate on Ir(110)-(1 $\times$ 2) is a consequence of the corrugation of this surface rather than, for example, the presence of a particular, disordered carbonaceous residue on the surface. A very plausible intermediate in  $n\text{-C}_4\text{H}_{10}$  hydrogenolysis over Ir(110)-(1 $\times$ 2) is a metallacycle pentane. For example, it is known that transition-metal homogeneous complexes containing metallacycle pentane ligands can decompose thermally to two  $\text{C}_2\text{H}_4$  ligands,<sup>21</sup> which would be hydrogenated to  $\text{C}_2\text{H}_6$  under our experimental conditions, in agreement with the observed selectivity. The corollary to this hypothesis is that metallacycle pentane formation is favored on those surfaces that contain low-coordination-number metal atoms, and which is *necessary* from a stereochemical point of view on the two single-crystalline surfaces discussed here.

To summarize, the selectivity for  $\text{C}_2\text{H}_6$  production from the hydrogenolysis of  $n\text{-C}_4\text{H}_{10}$  over Ir catalysts scales with the concentration of low-coordination-number metal surface atoms. This observation and detailed interpretation are limited neither to  $n\text{-C}_4\text{H}_{10}$  nor to Ir, however. Rather, they serve to illustrate the profound importance of local surface structure in dictating the occurrence of particular reaction intermediates and, hence, catalytic *selectivity*.

Registry No. Ir, 7439-88-5; butane, 106-97-8.

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### Intramolecular [6 + 4] and [4 + 2] Tropone-Olefin Cycloaddition Reactions. Facile Synthesis of the Ingenane Ring System

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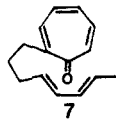
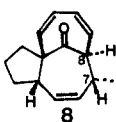
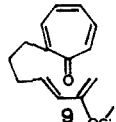
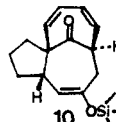
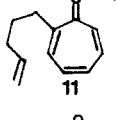
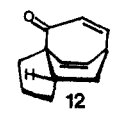
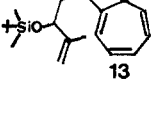
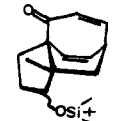
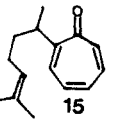
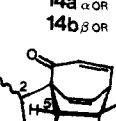
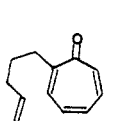
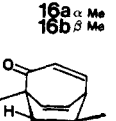
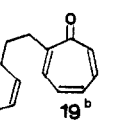
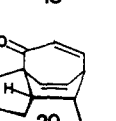
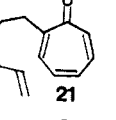
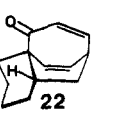
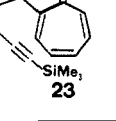
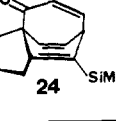
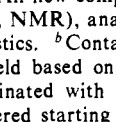
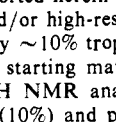
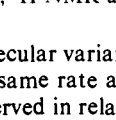
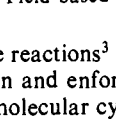
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The intermolecular [6 + 4] and [4 + 2] cycloaddition reactions of tropone with dienes and monoenes, respectively, have been extensively examined<sup>1</sup> and exploited in recent synthetic endeavors.<sup>2</sup> Surprisingly, there has not been an investigation of the intra-

Table I. Cyclizations of 2-Alkenyltropone

2-Alkenyltropone	Cycloadduct	Conditions	Yield % <sup>a</sup>
		150°/36 h	88
		80°/6 h	92
		150°/36 h	81
		200°/60 h 3:1 14a:14b	86
		240°/72 h 5:1 16a:16b	85
		0.1 eq. Et <sub>2</sub> AlCl 110°/30 h	80
		200°/72 h	77
		0.1 eq. Et <sub>2</sub> AlCl 110°/12 h	78 <sup>c</sup>
		150°/50 h	82 <sup>d</sup>
		180°/60 h	85 <sup>e</sup>
		150°/96 h	67

<sup>a</sup> All new compounds reported herein exhibited satisfactory spectral (IR, NMR), analytical, and/or high-resolution mass spectral characteristics. <sup>b</sup> Contaminated by ~10% tropone 17 (<sup>13</sup>C NMR analysis). <sup>c</sup> Yield based on recovered starting material (4%) and product contaminated with 18 (6%, <sup>1</sup>H NMR analysis). <sup>d</sup> Yield based on recovered starting materials (10%) and product contaminated with 18 (3%, <sup>1</sup>H NMR analysis). <sup>e</sup> Yield based on recovered 21 (42%).

molecular variant of these reactions<sup>3</sup> which should be subject to the same rate acceleration and enforcement of regioselectivity observed in related intramolecular cycloaddition processes. An additional stimulus for this study is illustrated in Scheme I. Namely, the cyclization of appropriately functionalized 2-alkenyltropone should provide rapid access to the carbocyclic frameworks of the tumor promoter ingenol<sup>4</sup> (3), via an intra-

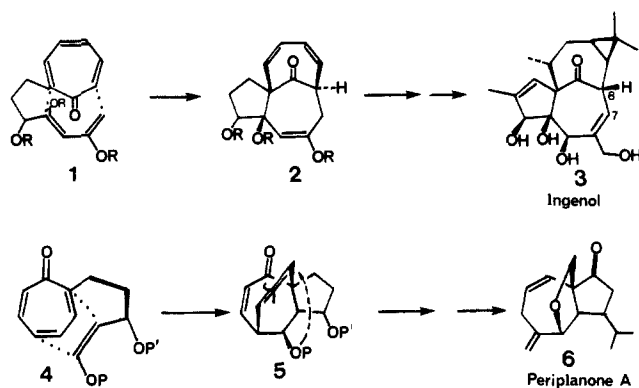
(3) While this manuscript was in preparation, two examples of intramolecular tropone-olefin cyclizations surfaced. (a) An intramolecular [6 + 4] cycloaddition: Rigby, J. H., personal communication. (b) An intramolecular [6 + 2] cycloaddition of an alkenyl tropone: Feldman, K. S.; Come, J. H.; Kosmider, B. J.; Smith, C. M. *Abstracts of Papers*, 190th National Meeting of the American Chemical Society, Chicago, IL; American Chemical Society: Washington, DC, 1985; ORGN 204.

\* Fellow of the Alfred P. Sloan Foundation, 1985-1987.

(1) For a review, see: (a) Pietra, F. *Chem. Rev.* **1973**, *73*, 293. For recent investigations and leading references, see: (b) Uyehara, T.; Kitahara, Y. *Bull. Soc. Chem. Jpn.* **1979**, *52*, 3355. (c) Garst, M. E.; Roberts, V. A.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 3882. (d) Garst, M. E.; Roberts, V. A.; Prussin, C. *Tetrahedron* **1983**, *39*, 581.

(2) (a) Rigby, J. H.; Sage, J.-M.; Raggon, J. *J. Org. Chem.* **1982**, *47*, 4815. (b) Uyehara, T.; Ogata, K.; Yamada, J.; Kato, T. *J. Chem. Soc., Chem. Commun.* **1983**, 17. (c) Garst, M. E.; Roberts, V. A.; Prussin, C. *J. Org. Chem.* **1982**, *47*, 3969.

Scheme I



molecular [6 + 4] cycloaddition (e.g., **1** → **2**), and the cockroach pheromone periplanone A<sup>5</sup> (**6**) which exploits the more common [4 + 2] cycloadditive process (**4** → **5**). We report herein that both types of intramolecular cycloaddition reactions proceed smoothly and stereospecifically.

We initially examined the intramolecular [6 + 4] cycloaddition<sup>6</sup> reactions of tropones **7** and **9'** (Table I). The cyclization of **7** was easily effected (150 °C, 36 h, toluene, 88%) to afford a single adduct **8**. The assigned stereochemistry is based on the well-known preference for the exo mode of cycloaddition in intermolecular troponone–diene [6 + 4] cycloadditions.<sup>1c,d</sup> In addition, the H7,H8 coupling constant of 10.4 Hz in the <sup>1</sup>H 360-MHz spectrum of **8** is clearly inconsistent with a dihedral angle of 70.6° (calculated by using the MM2 molecular mechanics program<sup>11</sup>) for the endo adduct and reasonable for the calculated 150.2° dihedral angle in **8**. The cycloaddition of **9** also afforded a single stereoisomer (92%) under milder conditions (80 °C, 6 h), in accord with a dominant troponone–LUMO, diene–HOMO frontier orbital interaction.<sup>1c,d</sup> It should be noted that these cycloadditions are also periselective in that none of the adducts derived from intramolecular [4 + 2] cycloaddition (vide infra) were observed.<sup>12</sup> Thus, the ingenane carbocyclic skeleton has been constructed in two steps from troponone. The utilization of this strategy in the total synthesis of ingenol (**3**) now seems justified and will require the attachment of a more highly oxidized diene to troponone, cf. troponone **1**, and the formidable adjustment of stereochemistry at C-8.

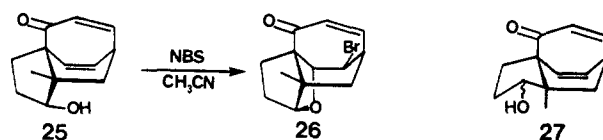
Our test case for examining intramolecular [4 + 2] troponone–olefin cycloadditions was troponone **11** (Table I). After thermolysis in a sealed tube (150 °C, 36 h, toluene) a single stereoisomer was isolated in good yield (77%) which is assumed to be the endo

adduct **12**. An examination of molecular models suggests that the endo transition state is less strained than the exo transition state. Moreover, the transition-state strain energy difference is estimated to be 2.1 kcal/mol by using MMPM,<sup>13</sup> a modified version of the MM2 molecular mechanics program. A Boltzmann distribution at 150 °C gives a predicted 92:8 endo:exo ratio.

The regio- and stereoselectivity as well as the facility of this intramolecular cycloaddition are noteworthy in comparison to an intermolecular cycloaddition we have examined. Specifically, the [4 + 2] cycloaddition of troponone (1.8 mmol) with 1-octene (18 mmol) in toluene (0.5 mL) affords mostly recovered troponone (52%) and a mixture of four products (4.6:3.5:3.4:1, 11%) under similar conditions (180 °C, 36 h).

Substitution of the dienophilic alkene moiety of **11** with alkyl groups retards the cycloaddition. Thus, the cyclizations of tropones **13**, **15**, and **17** took place only at relatively higher temperatures (200, 240, and 200 °C, respectively). However, these reactions were subject to Lewis acid catalysis and proceeded smoothly in the presence of catalytic amounts of Et<sub>2</sub>AlCl in refluxing toluene. To the best of our knowledge, these are the first examples of catalyzed troponone–olefin cycloadditions<sup>14</sup> and are unique from a mechanistic standpoint since the *diene*, instead of the *dienophile*, is activated for the cycloaddition which in this case is an inverse electron demand Diels–Alder reaction.<sup>1b</sup> An alternative mechanism involving the nonconcerted, stepwise cyclization of the olefinic side chain with a tropylium ion intermediate can be eliminated since the cyclizations of **17** and **19** were stereospecific, i.e., no appreciable product crossover was detected.

Finally, the relative asymmetric induction observed in the cyclization of **13** is remarkably amplified when the Lewis acid is present.<sup>15</sup> The factor(s) responsible for this effect are not clear at the moment; however, the stereochemical assignments are firm. Hydrolysis of the silyl ethers **14** gave a mixture of alcohols which were separated by HPLC. The major alcohol, **25**, gave the bromo ether **26** upon treatment with NBS (1.1 equiv, room temperature, 1 h, CH<sub>3</sub>CN, 86%), whereas the minor isomer remained unchanged under these conditions. [The alcohol **25** could be regenerated from **26** with zinc in acetic acid (50%).] The dia-



stereomeric alcohols **27**, derived from cycloaddition of **13** via the exo transition state, are clearly incapable of producing bromo ethers resulting from cyclization with the unconjugated double bond. Thus, the endo stereochemical assignment for this particular case is secure and lends support for the additional stereochemical assignments for the [4 + 2] cycloadducts in Table I.

In summation, the general success of intramolecular [6 + 4] and [4 + 2] troponone–olefin cycloadditions has been demonstrated. The further investigation of these reactions and their exploitation in natural product synthesis<sup>15</sup> outlined in Scheme I is under way

(4) For a synthetic approach to ingenol and references concerning its outstanding biological properties, see: Paquette, L. A.; Nitz, T. J.; Ross, R. J.; Springer, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 1446.

(5) Talman, E.; Verwiel, P. E. J.; Ritter, F. J.; Persoons, C. *J. Isr. J. Chem.* **1978**, *17*, 227.

(6) For other types of intramolecular [6 + 4] cycloadditions, see: Houk, K. N.; Doa, M. J.; Gupta, Y. N. *J. Am. Chem. Soc.* **1982**, *104*, 7336. (b) Houk, K. N.; Gupta, Y. N.; Mareda, J.; Wu, T.-C. *Ibid.* **1983**, *105*, 6996.

(7) All of the 2-substituted tropones<sup>8</sup> in Table I were prepared from troponone<sup>9</sup> by a one-pot procedure developed in our laboratories. Analogous to Grignard and organolithium reagents,<sup>8c,d,e,10</sup> lithio sulfone monoanions smoothly participate in 1,8-addition reactions with troponone (−78 °C, 30 min.) to provide intermediate dihydrotroponone adducts after protonation with acetic acid (1.1 equiv, −78 °C). DBU (2 equiv) is then added to the reaction mixture in order to promote elimination of phenylsulfonic acid and subsequent aromatization to the desired 2-substituted troponone. Full experimental details will be reported separately.

(8) (a) Brady, W. T.; Hieble, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 4278. (b) Noyori, R.; Takaya, H.; Hayakawa, Y.; Makino, S. *Ibid.* **1978**, *100*, 1778. (c) Bickel, A. F.; van Helden, R.; ter Borg, A. P. *Recl. Trav. Chim. Pays-Bas* **1962**, *81*, 591. (d) Nozoe, T.; Mukai, T.; Murata, I. *Proc. Jpn. Acad.* **1953**, *29*; *Chem. Abstr.* **1955**, *49*, 996. (e) Hiskey, C. F.; Doering, W. v. E. *J. Am. Chem. Soc.* **1952**, *74*, 5688.

(9) (a) Radlick, P. *J. Org. Chem.* **1964**, *29*, 960. (b) Reingold, I. D.; DiNardo, L. *J. Ibid.* **1982**, *47*, 3544.

(10) (a) Chapman, O. L.; Pasto, D. J.; Griswold, A. A. *J. Am. Chem. Soc.* **1962**, *84*, 1213. (b) Nozoe, T.; Mukai, T.; Tezuka, T. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 619.

(11) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(12) Steric effects may contribute to this periselectivity. Thus, the [4 + 2] cycloaddition of troponone **17**, which also possesses a trans-substituted dienophile, does not take place at temperatures in the range of 150 °C. In addition, electronic effects may be involved. There is an antibonding interaction between the lobes on C-6 and C-6' in the frontier orbitals of the bridge-endo transition state for the [4 + 2] cycloaddition reactions of **7** and **9**.

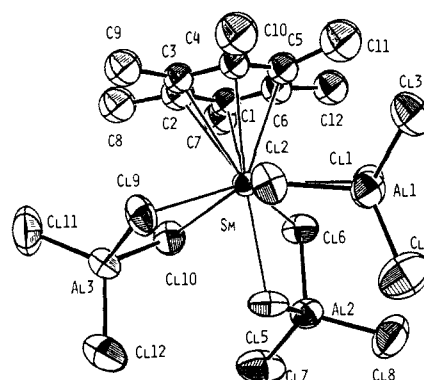
(13) We used the MMPM program as parameterized, available from Serena Software, Bloomington, IN 47401. As a first approximation, transition-state bond orders of 0.3 (2.26 Å) were entered which gave transition-state bond lengths and torsional angles very similar to those obtained from the more rigorous calculation for the butadiene–ethylene cycloaddition (Houk, K. N.; Brown, F. K. *Tetrahedron Lett.* **1984**, *41*, 4609). Moreover, the transition-state strain energy difference is approximately the same as the product SE (SE<sub>exo</sub> - SE<sub>endo</sub> = 2.7 kcal/mol). Calculations were performed on an IBM-XT with 640 K core and a 8087 chip. We are indebted to Professor J. Gajewski of the University of Indiana for fruitful discussions and helpful advice.

(14) For an unsuccessful attempt to catalyze troponone reactions with 2,3-dimethyl-1,3-butadiene and 1-[(trimethylsilyloxy)-1,3-butadiene, see ref 1d.

in our laboratories.

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(15) We have shown that the diastereomers **14a,b** are epimeric at the (*tert*-butyldimethylsilyloxy-bearing carbon, as opposed to endo/exo diastereomers, by obtaining the same diketone upon hydrolysis of **14a,b** (HF,  $\text{CH}_3\text{CN}$ ) separation of the resulting keto alcohols, and subsequent oxidation (PCC). We have also shown that the diastereomers **16a** and **16b** are epimeric at the tertiary carbon bearing the methyl substituent by converting them to the cedranoids  $\beta$ - and  $\alpha$ -pizitol, respectively (unpublished results).



**Figure 1.** ORTEP drawing of  $\text{Sm}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_3$ . All atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

### $\text{Sm}(\eta^6\text{-C}_6\text{Me}_6)(\eta^2\text{-AlCl}_4)_3$ : The First Structure of a Rare Earth Complex with a Neutral $\pi$ -Ligand

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The nature of the metal centers in most rare earth and actinide compounds has been recognized to approximate the ionic limit.<sup>1a</sup> An intriguing anomaly in this otherwise consistent behavior is the relative ease with which vapors of some f-block metal halides form intercalation phases with graphite.<sup>1b,2</sup> Clearly, a favorable interaction between the aromatic graphite layers and the metal halides must exist, viz., some form of  $\pi$ -bonding.

We and others have demonstrated before that one of these intercalators,  $\text{UCl}_4$ , can undergo arylation reactions to yield  $\eta^6$ -arene complexes and we have structurally characterized such compounds of U(IV)<sup>3,4</sup> and U(III).<sup>5,6</sup> In light of the fact that U arene complexes are the only examples of neutral  $\pi$ -ligands bonded to f-elements, we were wondering whether uranium constitutes a special case and whether an f-orbital contribution was instrumental in the bonding. It was therefore tempting to challenge our synthetic approach with lanthanide metals for which there is no structurally characterized complex with neutral  $\pi$ -ligands on record. We have chosen a known intercalator of graphite and wish to report here on the first arene complex of a rare earth element,  $\text{Sm}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_3$ -1. Stoluene, (**1**).

The reaction of  $\text{SmCl}_3$ ,  $\text{AlCl}_3$  and hexamethylbenzene (hmb) in refluxing toluene in the presence of pieces of Al foil leads to a blood red solution (indicative of a Sm(II) compound) and complete dissolution of the salts within 20 min. The hot solution is filtered and very slowly cooled to room temperature. Yellow plates of the title compound deposit over a period of 2 days. Several batches were collected by filtration. The collection was discontinued when a tarry red residue started precipitating together with the title compound. This tar is insoluble in all solvents which are nondestructive for **1** and therefore impossible to separate. The total isolated yield of pure **1** was 14%. Addition of  $\text{CH}_2\text{Cl}_2$  to the red solution results in a color change to yellow within 3 h but

**Table I.** Geometric Properties of f-Element-Arene Complexes

compound	M-Cl, Å	M-C, Å	ionic radius	ref
$\text{U}(\eta^6\text{-C}_6\text{H}_6)(\eta^2\text{-AlCl}_4)_3$	2.88 [3] <sup>a</sup>	2.91	1.025	5
$[\text{U}(\text{C}_6\text{Me}_6)\text{Cl}_2(\mu\text{-Cl})_3\text{-U}(\text{C}_6\text{Me}_6)\text{Cl}_2]$	2.75 [5] <sup>b</sup> 2.58 [1] <sup>c</sup>	2.92 [4]	0.93	3
$(\text{C}_6\text{Me}_6)\text{UCl}_2(\mu\text{-Cl})_3\text{UCl}_2\text{-}(\mu\text{-Cl})_3\text{UCl}_2(\text{C}_6\text{Me}_6)$	2.78 [8] <sup>b</sup> 2.53 [1] <sup>c</sup>	2.94 [3]	0.93	4
$[\text{U}_3(\mu^3\text{-Cl})_2(\mu^2\text{-Cl})_3\text{-}(\mu^1, \eta^2\text{-AlCl}_4)(\eta^6\text{-C}_6\text{Me}_6)_3]$	2.78 [2] <sup>b</sup> 2.99 [9] <sup>d</sup> 2.94 [3] <sup>a</sup>	2.92 [4]	1.025	6
$\text{Sm}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_3$	2.85 [2] <sup>a</sup>	2.89 [5]	0.964	this work

<sup>a</sup>  $\eta^2\text{-AlCl}_4$ . <sup>b</sup> Bridging. <sup>c</sup> Terminal. <sup>d</sup> Capping.

only impure products have so far been obtained. Although **1** formally was not involved in the reduction process attempts to prepare it directly have so far afforded only powders of erratic composition in very low yields. If, on the other hand, reflux is continued for longer time periods the yields of **1** decrease, probably in favor of the red compound which is presently under investigation.

$\text{Sm}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_3$  is a molecular complex (Figure 1).<sup>7</sup> The coordination polyhedron is a distorted pentagonal bipyramid with the arene in an apical position. The arrangement is similar to that reported for  $\text{U}(\text{C}_6\text{H}_6)(\text{AlCl}_4)_3$ .<sup>5</sup> The mean Sm-Cl and Sm-C distances are 2.85 [2] and 2.89 [5] Å, respectively. There is no statistically significant distortion of the hmb moiety.

Table I summarizes some metric properties of f-element-arene complexes. Although the differences in the lengths of comparable bonds are not significant in a statistical sense there are some interesting trends. In agreement with the difference of the ionic radii of Sm(III) and U(III), we find that the M- $\eta^2\text{-AlCl}_4$  and M- $\eta^6\text{-C}_6\text{Me}_6$  bonds are shorter in the Sm(III) compound, albeit by less than the differences in the ionic radii. The M-C mean distances in the U(IV) complexes, on the other hand, are systematically longer than those in either the Sm(III) or U(III) complexes. Not taking packing forces into account, this would indicate that the M-arene bonds are somewhat stronger in the trivalent compound.

Although arene bonding in actinides and lanthanides has not yet been rationalized by calculations supported by spectroscopy, we can now be confident that f-orbital contribution does not play an important role because the f-shells in lanthanide metals are efficiently screened by the closed  $5s^2$  and  $5p^6$  shells. Therefore, combinations of 5d, 6s, and 6p orbitals are assumed to be the

(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; pp 981-1046. (b) *Ibid.*; pp 359-361.

(2) *Gmelin Handbuch der anorganischen Chemie: Sc, Y, La-Lu*, 8th ed.; Springer Verlag: Berlin, 1982; Part C 4a.

(3) Cotton, F. A.; Schwotzer, W. *Organometallics* 1985, 4, 942.

(4) Campbell, G. C.; Cotton, F. A.; Haw, J. F.; Schwotzer, W. *Organometallics* 1986, 5, 274.

(5) Cesari, M.; Pedretti, U.; Zazetta, A.; Lugli, G.; Marconi, N. *Inorg. Chim. Acta* 1971, 5, 439.

(6) Cotton, F. A.; Schwotzer, W.; Simpson, C. Q. *Angew. Chem., Int. Ed. Engl.*, in press.

(7) Crystal data:  $\text{SmCl}_3\text{Al}_3\text{C}_7\text{H}_{18}\cdot 1.5\text{C}_7\text{H}_8$ ; monoclinic  $P2_1/c$ ;  $a = 18.696$  (4) Å,  $b = 16.906$  (3) Å,  $c = 12.262$  (2) Å,  $\beta = 100.81$  (2)°,  $V = 3807$  (2) Å<sup>3</sup>,  $Z = 4$ ;  $R = 5.2\%$ ,  $R_w = 6.1\%$ . A table with information pertaining to data collection and refinement and a list of fractional coordinates are available as supplementary material.