

Figure 1. NMR spectrum (C_6D_6 , 300 MHz) of $Ru(TTP)(CHCH_3)$.

When $[Ru(TTP)]_2$ is treated with a slight excess of $N_2CHCO_2CH_2CH_3$ in benzene at room temperature the carbene complex $Ru(TTP)(CHCO_2CH_2CH_3)$ (**6**) is produced.⁹ The ethyl triplet and quartet resonances each appear ca. 1 ppm upfield from those in free ethyl diazoacetate. The carbene proton resonance is observed at 13.43 ppm, within the range for the proton in complexes of the form $M=C(H)R$.¹⁰ The eight β -pyrrolic protons appear as a singlet, indicating that the carbene complex has axial symmetry on the NMR time scale at room temperature. An electronic barrier to rotation would not be expected since either of the symmetry equivalent metal d_{xz} or d_{yz} orbitals can participate in the π -bonding.

Treatment of a benzene or THF solution of the dimer with a stream of nitrogen containing diazoethane produces the ethylidene complex $Ru(TTP)(CHCH_3)$ (**7**).¹¹ The 1H NMR spectrum of this complex in C_6D_6 is shown in Figure 1. The ethylidene ligand gives rise to a doublet at -2.55 ppm for the methyl group and a quartet at 13.03 ppm for the carbene proton. Irradiation of the quartet at 13.03 ppm causes the doublet at -2.55 ppm to collapse to a singlet. The phenyl protons on the *p*-tolyl substituents on the porphyrin appear in the 1H NMR as four distinct doublets, indicating inequivalence of the two sides of the porphyrin plane. When the ethylidene complex is generated in THF solution a small amount of the ethylene complex **5** is observed by 1H NMR, suggesting that some rearrangement of the ethylidene fragment may have occurred. The carbene complexes described herein are the first such metalloporphyrin species to contain a proton on the carbene carbon atom.

These results implied that reaction with diazomethane might lead to a methylene complex " $Ru(TTP)(CH_2)$ ". However, when CH_2N_2/N_2 is bubbled through a THF solution of $[Ru(TTP)]_2$ a methylene species is not observed. Instead, 1H NMR shows the reaction products to be a 1:1 mixture of the ethylene complex **5** and $Ru(TTP)(THF)_2$ (**2**), as shown in Scheme I. The bimolecular coupling of $M=CH_2$ fragments to form $M(CH_2=CH_2)$ and $M(solvato)$ species is not unprecedented.¹² The stoichiometry of the reaction observed here is consistent with such a process, although as yet we have no direct evidence for the involvement of $Ru=CH_2$ intermediates.

(9) We prefer the formulation generally adopted for late-transition-metal carbene complexes; in this case $Ru(II)$ bonded to a formally neutral carbene fragment. $Ru(TTP)(CHCO_2CH_2CH_3)$ NMR (C_6D_6 , 300 MHz) H_β 8.78 (s), H_o, H_m 8.13 (d), 8.07 (d) 7.33 (d), 7.24 (d), $PhCH_3$ 2.40 (s), CH 13.43 (s), CH_2CH_3 2.53 (q), CH_2CH_3 0.14 (t) ppm; UV-vis (C_6H_6) λ_{max} (log ϵ), 408 (4.96), 529 (4.02) nm.

(10) (a) Marsella, J. A.; Foltling, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596-5598. (b) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31-C36.

(11) $Ru(TTP)(CHCH_3)$ NMR (C_6D_6 , 300 MHz) H_β 8.73 (s), H_o, H_m 8.14 (d), 8.05 (d), 7.33 (d), 7.23 (d), $Ph-CH_3$ 2.39 (s), $CHCH_3$ 13.03 (q), $CHCH_3$ -2.55 (d) [$J(CHCH_3) = 6$ Hz] ppm; MS (NDCI), m/z [M]⁻ 798, [$M - CHCH_3$]⁻, base peak 770; UV-vis (C_6H_6) λ_{max} (log ϵ), 395 (4.82), 421 (4.97), 527 (4.14) nm.

(12) (a) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811-5819. (b) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577-6578.

A second class of neutral carbene precursors is the Wittig reagents $Ph_3P=CRR'$, which have been successfully used to transfer a carbene moiety to a transition metal.¹³ We are currently investigating the utility of such species as reagents for the preparation of ruthenium porphyrin carbene complexes.

The magnetic properties and formal metal-metal double bond of the $[M(Por)]_2$ dimer can be satisfactorily modeled by an MO scheme in which the HOMO's and LUMO's are derived from metal d orbitals.² The presence of the half empty π^* and empty σ^* orbitals implies that reduction of the dimer by a total of four electrons would result in a net bond order of zero and is consistent with cleavage of the dimer to form two zerovalent dianionic monomers.

$[Ru(Por)]_2$ (Por = OEP, TTP), when stirred with Na/K alloy in THF for 30 min, or K metal in THF for several hours, gives a suspension of a violet-black precipitate, which is decanted from the reducing agent. This insoluble, highly air-sensitive material has been characterized on the basis of its subsequent reactivity as the ruthenium(0) porphyrin dianion $K_2[Ru(Por)]$. For example, treatment of $K_2[Ru(TTP)]$ (**8**) with 1,2-dibromoethane in THF yields the same ethylene complex **5** that was formed independently in the reaction of $[Ru(TTP)]_2$ with ethylene (Scheme I).

The osmium dimer $[Os(TTP)]_2$ can be reduced under the same conditions to yield the sparingly soluble green salt $K_2[Os(TTP)]$. The 1H NMR spectrum of this complex is consistent with a diamagnetic species and indicates that the plane of symmetry which contains the porphyrin is retained.¹⁴ The reactions of the ruthenium and osmium dianions are the subject of another publication.¹⁵

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(13) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43-51.

(14) $K_2[Os(TTP)]$ NMR (THF- d_8 , 300 MHz) H_β 8.93 (s), H_o, H_m 7.91 (d), 7.33 (d), CH_3 2.50 (s) ppm.

(15) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E., unpublished results.

Zirconium Cluster Compounds Stabilized by Interstitial Atoms

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A prolific cluster chemistry has been discovered for electron-poorer zirconium analogues of the traditional $(Nb, Ta)_6X_{12}^{n+}$ clusters ($X = Cl, Br, \text{some } I, n = 2, 3, 4$)^{1,2} where a second-period element Be, B, C, or N within each cluster now contributes both strong Zr-interstitial (int) bonding and additional electrons. The results of an extensive study of Zr-Cl-int systems to explore the breadth and variety of this chemistry has given the results summarized in Table I according to the structural framework, i.e., without regard to interstitial atoms and cations. All compounds except $Zr_6Cl_{14}B$ are obtained in greater than 90% yield as red-brown powders or reddish-black, well-faceted gemlike crystals by stoichiometric reactions of Zr powder, $ZrCl_4$, and, as appro-

(1) Schäfer, H.; Schnering, H.-G. *Angew. Chem.* **1964**, *76*, 833.

(2) Wells, A. F. "Structure Inorganic Chemistry", 5th ed., pp. 432-437, Clarendon Press: Oxford, England 1984; pp. 432-437.

(3) Guthrie, D. H.; Corbett, J. D. *Inorg. Chem.* **1982**, *21*, 3290.

(4) Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.*, submitted for publication.

(5) Bauer, D.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1968**, *361*, 259.

(6) Imoto, H.; Simon, A., unpublished results.

Table I. 14-Electron, Centered Clusters of Zirconium

struct type	new isostructural compds	cluster connectivity ^a	space group	lattice params, Å
$Zr_6I_{12}C^b$	$Zr_6Cl_{12}Be$	$[Zr_6Cl^i_6Cl^{i-a}_{6/2}]Cl^{i-a}_{6/2}$	$R\bar{3}$, hexagonal	$a = 13.161$ (1) $c = 8.840$ (1)
	$Zr_6Br_{12}B$ (15) ^c			$a = 13.623$ (1) $c = 9.307$ (1)
$KZr_6Cl_{13}Be$	$KZr_6Cl_{13}Be^d$	$[Zr_6Cl^i_{10}Cl^{i-1}_{2/2}]Cl^{i-a}_{6/3}$	$Pnmm$, orthorhombic	$a = 11.627$ (2) $b = 12.139$ (2) $c = 7.472$ (1)
	$Zr_6Cl_{13}B$			$a = 11.523$ (2) $b = 12.142$ (2) $c = 7.422$ (1)
	$Zr_6Br_{13}B$			$a = 12.074$ (1) $b = 12.6767$ (8) $c = 7.7343$ (7)
$Nb_6Cl_{14}^e$	$Zr_6Cl_{14}C^f$	$[Zr_6Cl^i_{10}Cl^{i-a}_{2/2}]Cl^{i-1}_{2/2}Cl^{i-a}_{4/2}$	$Cmca$, orthorhombic	$a = 14.022$ (2) $b = 12.563$ (2) $c = 11.475$ (3)
	$Zr_6Cl_{14}B^d$ (13)			$a = 14.243$ (1) $b = 12.640$ (2) $c = 11.546$ (1)
	$(Cs-Na)Zr_6Cl_{14}B$			
$Ta_6Cl_{15}^g$	$Zr_6Cl_{15}N^d$	$[Zr_6Cl^i_{12}]Cl^{i-a}_{6/2}$	$Ia\bar{3}d$, cubic	$a = 21.171$ (1)
	$Na_{0.5}Zr_6Cl_{15}C^d$ (13.5)			$a = 21.466$ (1)
$CsNb_6Cl_{15}^h$	$Na_2Zr_6Cl_{15}B$	$[Zr_6Cl^i_{12}]Cl^{i-a}_{6/2}$	$Pmma$, orthorhombic	$a = 21.685$ (4)
	$(Cs,Rb)Zr_6Cl_{15}C$			$a = 18.489$ (5) $b = 13.909$ (3) $c = 9.690$ (3)
	$KZr_6Cl_{15}C^{d,i}$			$a = 18.672$ (4) $b = 14.026$ (4) $c = 9.731$ (2)
	$CsKZr_6Cl_{15}B^{d,i}$			$a = 11.386$ (1) $b = 15.980$ (1) $c = 14.008$ (1)
$K_2Zr_6Cl_{15}B$	$K_2Zr_6Cl_{15}B^d$	$[Zr_6Cl^i_{12}]Cl^{i-a}_{6/2}$	$Cccm$, orthorhombic	$a = 13.251$ (1) $b = 14.319$ (1) $c = 14.092$ (2)
$Na_4Zr_6Cl_{16}Be$	$Na_4Zr_6Cl_{16}Be^d$	$[Zr_6Cl^i_{12}]Cl^{i-a}_{4/2}Cl^a_2$	$Pccn$, orthorhombic	

^a Connectivity description: ref 1: Cl^i is edge-bridging within a Zr_6Cl_{12} cluster, Cl^a is terminal to a Zr vertex, and double indices refer to mixed functions. ^b First reported as Zr_6I_{12} .^{3,4} ^c Electron count if different from 14. ^d Single-crystal structural refinement; all others were defined on the basis of Guinier powder patterns. ^e Simon, A.; von Schnering, H.-G.; Wöhrle, H.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1965**, *339*, 155. ^f Refined as the iodide.⁴ ^g Reference 5. ^h Reference 6. ⁱ Alternate cation site occupied.

appropriate, M^iCl , C, B, Be, or $ZrNCl$ in sealed Ta tubing at 700–860 °C for 2–3 weeks.⁷ Black gems of $Zr_6Cl_{14}B$ are formed near 950 °C in about 10% yield together with $Zr_6Cl_{13}B$ and Zr_2Cl_2B .

An extraordinary diversity of compounds and structure types is accessible through the use of various combinations of small nonmetal interstitials, cations (size and number), and degree of reduction, including three new structure types involving Zr_6X_{13} , Zr_6X_{15} , and Zr_6X_{16} stoichiometries (Table I).⁷ $KZr_6Cl_{13}Be$ and $Na_4Zr_6Cl_{16}Be$ represent new stoichiometries and connectivities for M_6X_{12} -type clusters, whereas $K_2Zr_6Cl_{15}B$ is a new arrangement of the M_6X_{15} connectivity⁵ with one-third of the Zr- Cl^a -Zr bridges linear. In addition, two new variations of the $CsNb_6Cl_{15}$ structure⁶ are seen in $KZr_6Cl_{15}C$ and $CsKZr_6Cl_{15}B$. The former uses an alternate cation site while the latter shows occupation of both sets of cation sites. The reported phases Zr_6I_{12} and $CsZr_6I_{14}$ ³ are also known to contain strongly bound and stoichiometric amounts of interstitial carbon.⁴

The following are observed: (1) A wide variety of second-period elements can be used to stabilize Zr_6Cl_{12} clusters; (2) nearly all of the clusters contain 14 e^- for Zr–Zr and Zr–int bonding; (3) the Zr–int distances increase from N to Be as expected on the basis of covalent radii; (4) the M_6X_{15} structures are all very similar in energy with the cation number and size being the primary factors in determining the structure.

The most novel new structure is clearly $KZr_6Cl_{13}Be$, not only because of its unprecedented stoichiometry but also because of two key structural features. The cluster framework, Figure 1, is built up of linear strings of Zr_6Cl_{12} clusters sharing trans, inner chlorines. These $\frac{1}{2}[Zr_6Cl^i_{10}Cl^{i-1}_{2/2}]$ units are further connected

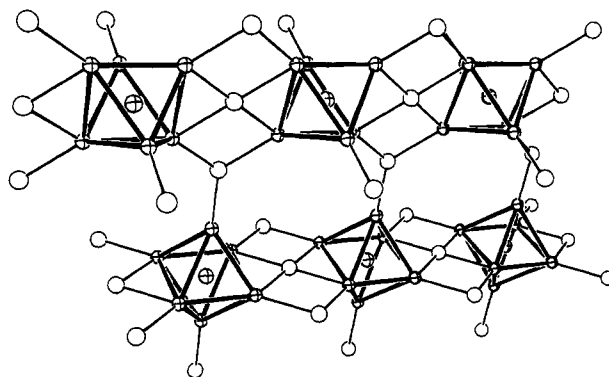


Figure 1. Interconnectivity of Zr_6Cl_{12} clusters in $KZr_6Cl_{13}Be$. Heavy lines define the beryllium-centered zirconium octahedra, while chlorine atoms are shown as open ellipsoids. Edge-bridging Cl^i not involved in intercluster bonding have been omitted. Thermal ellipsoids are at the 90% probability level.

into a three-dimensional array through triply shared exo chlorines. The former Cl^{i-1} connectivity has not been previously observed with clusters but is found between condensed cluster chains in the nonmetal-poorer Er_4I_5 , Er_6I_7 ,⁸ and $Sc_{0.75}Zn_{1.25}Mo_4O_7$ ⁹ structure types. The K^+ cations lie in channels between the linear strings of clusters. The phase $Na_4(Zr_6Cl_{12})Cl_4Be$ is probably best described as a distorted M_6X_{12} version of the $(Mo_6Cl_8)Cl_4$ structure.¹⁰

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(9) McCarty, R. E. *ACS Sym. Ser.* **1983**, *211*, 273.

(10) Schäfer, H.; von Schnering, H.-G.; Tillach, J.; Kühnen, F.; Wöhrle, H.; Baumann, H. *Z. Anorg. Allg. Chem.* **1967**, *353*, 281.

(7) Ziebarth, R. P.; Corbett, J. D., unpublished results.

Work is continuing on cation exchange, addition and removal as well as on the binding of other interstitial atoms.

Extended Hückel MO calculations carried out on isolated octahedral $Zr_6Cl_{18}^{4-}$ and $Zr_6Cl_{18}int^{n-}$ ($int = C, B, Be$) clusters⁷ reveal that four of eight Zr-Zr bonding orbitals in the empty cluster are stabilized by interaction with the interstitial's s and p orbitals and form four lower lying orbitals primarily responsible for Zr-int bonding (although these retain some Zr-Zr bonding character). There remain four unchanged Zr-Zr bonding orbitals, the energy of which are dependent only on the size of the cluster, and four Zr-int antibonding orbitals appear at high energies. For electron counting purposes, the interstitial atom can be considered to "donate" its valence electrons to the cluster MOs since the number of bonding orbitals is unchanged, although the interstitial is doubtlessly somewhat negative.⁴ The HOMO-LUMO gap for 14-electron clusters is calculated to be ~ 1.4 eV, consistent with the observed stability.

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Registry No. $Zr_6Cl_{12}Be$, 96929-11-2; $Zr_6Br_{12}B$, 96929-14-5; $KZr_6Cl_{13}Be$, 96929-12-3; $Zr_6Cl_{13}B$, 96929-13-4; $Zr_6Br_{13}Br$, 96948-42-4; $Zr_6Cl_{14}C$, 96929-15-6; $Zr_6Cl_{14}B$, 96929-16-7; $Zr_6Cl_{15}N$, 96948-43-5; $Na_2Zr_6Cl_{15}C$, 96929-20-3; $KZr_6Cl_{15}C$, 96929-22-5; $CsKZr_6Cl_{15}B$, 96929-23-6; $K_2Zr_6Cl_{15}B$, 96929-24-7; $Na_4Zr_6Cl_{15}Be$, 96929-25-8; $Zr_6Cl_{18}^{4-}$, 96964-12-4; $Zr_6Cl_{18}C^{8-}$, 96929-26-9; $Zr_6Cl_{18}B^{7-}$, 96929-28-1; $Zr_6Cl_{18}Be^{2-}$, 96929-27-0; Zr, 7440-67-7; $ZrCl_4$, 10026-11-6; NaCl, 7647-14-5; CsCl, 7647-17-8; KCl, 7447-40-7; C, 7440-44-0; B, 7440-42-8; Be, 7440-41-7; ZrNCl, 13932-08-6.

Supplementary Material Available: Structural parameters and refinement data for $KZr_6Cl_{13}Be$ (1 page). Ordering information is given on any current masthead page.

Methylaluminum Bis(2,6-di-*tert*-butyl-4-alkylphenoxide). A New Reagent for Obtaining Unusual Equatorial and Anti-Cram Selectivity in Carbonyl Alkylation

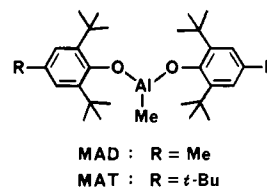
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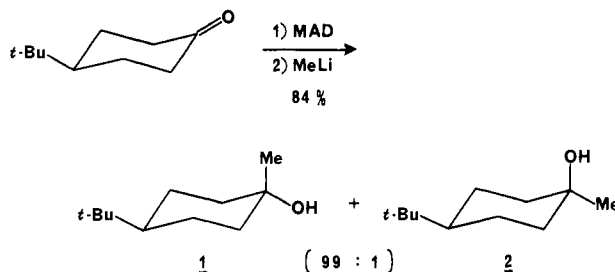
The carbonyl alkylation process has long been studied, and constitutes one of the most fundamental bond constructions in organic synthesis.¹ In contrast to the recent, extensive efforts in this area for the development of a stereoselective alkylation agent for obtaining axial alcohols from cyclohexanones,² there exists no reliable methodology available for the selective synthesis of equatorial alcohols.³ Here we describe a *conceptually new approach* to this problem which involves a bulky organoaluminum compound, methylaluminum bis(2,6-di-*tert*-butyl-4-methylphen-

oxide)⁴ or methylaluminum bis(2,4,6-tri-*tert*-butylphenoxide)



(abbreviated to MAD or MAT, respectively), as a key reagent for stereoselective activation of a carbonyl moiety.

MAD can be prepared in situ from trimethylaluminum and 2,6-di-*tert*-butyl-4-methylphenol (molar ratio, 1:2) in toluene at room temperature for 1 h.⁴ Treatment of 4-*tert*-butylcyclohexanone with MAD (3 equiv) in toluene and subsequent addition



of methyl lithium in ether at -78 °C gave rise to a mixture of isomeric methyl carbinols in 84% yield, 99% of which was found to be equatorial alcohol 1.⁵ Use of MAT gave the similar stereoselectivity ($ax/eq = 0.5:99.5$).⁶ Methyl lithium solely is reported to undergo preferential equatorial attack to furnish the axial/equatorial ratio of 79:21.^{2a} While MAD and MAT have proved to be most satisfactory, some variation in the reagent was studied in detail under the similar conditions. Accordingly, the reaction of 4-*tert*-butylcyclohexanone with methyl lithium in the presence of modified organoaluminum reagents⁷ producing the axial and equatorial alcohols 2 and 1 gives the following axial/equatorial ratios: Me_2AlOPh (72:28); dimethylaluminum 2,4,6-trimethylphenoxide (69:31); dimethylaluminum 2,6-di-*tert*-butyl-4-methylphenoxide (5:95). The effect of exact stoichiometry in the reagent has also been examined and each 3 equiv of methyl lithium and MAD was found to be satisfactory.⁸

Some other examples are listed in Table I, which also includes the results in the absence of modified organoaluminum reagents for comparison. Clearly, MAD and MAT have played a crucial role for the stereoselective synthesis of hitherto unaccessible equatorial alcohols from cyclohexanone systems.⁹ The use of simple Grignard reagents as nucleophile is also highly efficient and in certain cases the stereoselection is virtually complete.¹⁰

(4) Starowieyski, K. B.; Pasykiewicz, S.; Skowrońska-Ptasińska, M. *J. Organomet. Chem.* 1975, 90, C43.

(5) The typical experimental procedure is provided by the methylation of 4-*tert*-butylcyclohexanone (entry 3 in Table I). To a solution of 2,6-di-*tert*-butyl-4-methylphenol (1.322 g, 6 mmol) in toluene (10 mL) was added a 2 M hexane solution of trimethylaluminum (3 mmol) and the resulting clear solution was stirred at room temperature for 1 h. The mixture was then cooled to -78 °C and 4-*tert*-butylcyclohexanone (154 mg, 1 mmol) followed by a 1.54 M ethereal solution of methyl lithium (3 mmol) was added at -78 °C. The solution was maintained at this temperature for 2 h. The reaction mixture was poured into 1 N HCl and the organic layer was washed with brine. The combined ether extracts were, after concentration, purified by column chromatography on silica gel to give a mixture of 1 and 2 (143 mg, 84% yield), the ratio of which was determined by GC on a 25-m PEG-HT capillary column to be 99:1.

(6) Since MAT easily solidifies in toluene, we used CH_2Cl_2 for the preparation of MAT.

(7) The modified organoaluminum reagents were prepared in situ from trimethylaluminum and the corresponding phenols in toluene at room temperature for 1 h.

(8) When 2 equiv each of methyl lithium and MAD was employed, a 1:99 mixture of axial and equatorial alcohols was obtained in 59% yield. With 1 equiv of the reagents the yield was further lowered to 31% in an ax/eq ratio of 2:98.

(9) Other strong Lewis acids such as $TiCl_4$ and $BF_3 \cdot OEt_2$ were not effective.

(1) Review: Ashby, E. C. *Chem. Rev.* 1975, 75, 521.

(2) Recent stereoselective syntheses of axial alcohols from cyclohexanones: (a) MacDonald, T. L.; Still, W. C. *J. Am. Chem. Soc.* 1975, 97, 5280. (b) Ashby, E. C.; Lin, J. J.; Watkins, J. J. *Tetrahedron Lett.* 1977, 1709. (c) Ashby, E. C.; Willard, G. F. *J. Org. Chem.* 1978, 43, 4094. (d) Ashby, E. C.; Noding, S. A. *Ibid.* 1979, 44, 4371. (e) Weidmann, B.; Seebach, D. *Helv. Chim. Acta* 1980, 63, 2451. (f) Weidmann, B.; Maycock, C. D.; Seebach, D. *Ibid.* 1981, 64, 1552. (g) Reetz, M. T. *Top. Curr. Chem.* 1982, 106, 1 and references cited therein.

(3) The previous attempt for equatorial alkylation with alkylaluminums was made by Ashby et al. (a) Laemmle, J. T.; Ashby, E. C.; Roling, P. V. *J. Org. Chem.* 1973, 38, 2526. (b) Ashby, E. C.; Laemmle, J. T. *ibid.* 1975, 40, 1469. Unfortunately, all organoaluminums except trimethyl- and triphenylaluminum gave large amounts of reduction product.