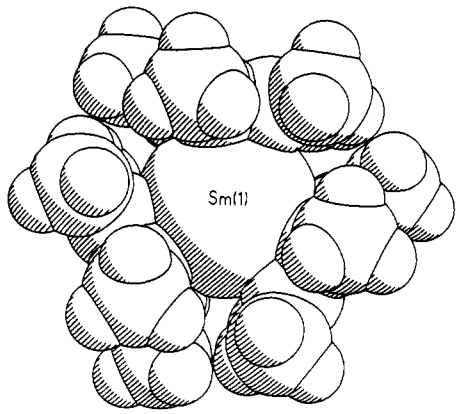

Figure 2. Space-filling model of $(C_5Me_5)_3Sm$ (2).

troid)-Sm-(ring centroid) angle is the smallest observed to date between two pentamethylcyclopentadienyl ligands in lanthanide complexes. Previously, the smallest observed angle, 127.0°, was found in $(C_5Me_5)_2Sm(C_5H_5)$ and the usual range is 130-138°.[7]

The rings are oriented to minimize the steric interactions as much as possible. The progression Sm-C(1) > Sm-C(2) > Sm-C(3) shows that each ring is tipped away from samarium such that the Sm-(ring centroid)-C(1) angle, 94.7°, is larger than the idealized 90° angle as well as the Sm-(ring centroid)-C(3) angle, 87.8°. The rings are oriented with respect to each other such that the C_5Me_5 carbon atom most distant from samarium in each ring (C(1)) is closest to the ring carbon atoms least distant from samarium in the next ring (the C(3)'s). The methyl groups are bent away from the center of the molecule such that the methyl carbon atoms lie out of the plane of the ring carbons by 0.17 (C(5)) to 0.52 Å (C(4)). These values can be compared to methyl group displacements of 0.09 to 0.31 Å in other $(C_5Me_5)_2Ln$ complexes.[22,23] This methyl group displacement causes the (ring centroid)-C(ring)-C(methyl) angles to deviate from 180° and again the angle involving C(4) is distorted most: Cn-C(1)-C(4), 162.3°; Cn-C(2)-C(5), 171.1°; Cn-C(3)-C(6), 166.5°.[23] These data demonstrate further the remarkable flexibility of the $(C_5Me_5)_2Sm$ unit to accommodate different ligand sets.[24]

The isolation of **2** has several implications for pentamethylcyclopentadienyl chemistry. First, the existence of **2** implies that a family of $(C_5Me_5)_3M$ complexes involving metals larger than Sm^{3+} should be sterically allowed. On the basis of Shannon radii,[25] $(C_5Me_5)_3M$ complexes may exist for M = La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Pm^{3+}, Th^{3+}, and U^{3+}. Since it is unknown if Sm^{3+} provides the limit in steric congestion in $(C_5Me_5)_3M$ complexes, it is possible that tris(pentamethylcyclopentadienyl) complexes may exist for smaller metals later in the lanthanide series, i.e., Eu^{3+} etc., as well as for other metals such as Th^{4+}, e.g., in a complex of the type $[(C_5Me_5)_3Th]^+$. Obviously, synthetic pathways to these compounds remain to be found.

The second implication involves the special reactivity of the pentamethylcyclopentadienyl-Sm^{2+} complexes.[9] In the past, the chemistry of $(C_5Me_5)_2Sm(THF)_{0-2}$ complexes was differentiated from that of other soluble Sm(II) complexes such as $SmI_2(THF)_2$,[26] $[(Me_3Si)_2N]_2Sm(THF)_2$,[27] and $[(Me_3Si)_2C_5H_3]_2Sm(THF)$[17] in that the latter complexes readily formed the tris(ligand) species (e.g., in reactions with CO), whereas $(C_5Me_5)_3Sm$ was not believed to exist.[4] Although formation of tris(ligand) complexes may be more facile for ligands smaller than C_5Me_5, eq 1 demonstrates that $(C_5Me_5)_3Sm$ can form under mild reaction conditions. Hence, the absence of ligand redistribution reactions leading to $(C_5Me_5)_3Sm$ cannot be a basis for the unusual chemistry observed.

Finally, despite the steric congestion in **2**, which may imply limited reactivity, $(C_5Me_5)_3M$ complexes may prove to have interesting chemistry. As shown in the space-filling model (Figure 2), access to the metal center is available via a channel down the $\vec{b}$ axis which may allow reactions with cylindrically symmetrical reagents of appropriate size. $(C_5Me_5)_3M$ complexes may also provide an opportunity to study reactions involving C_5Me_5 ring slippage. Studies in this direction are in progress.

Acknowledgment. We thank the National Science Foundation for support for this research. Funds for the purchase of the X-ray equipment were made available from NSF Grant CHE-85-14495.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (5 pages); listing of observed and calculated structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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Highly Stereo- and Regiocontrolled Cyclopentannulation via Allylphosphonate Conjugate Addition and Hydroboration-Oxidation-Elimination. Synthesis of Pentalenic Acid with Virtually Complete Stereo- and Regiocontrol

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Construction of complex carbon structures with a high degree of stereo- and regiocontrol, such as those in which the degree of stereoselectivity and/or regioselectivity in each pertinent step is ≥98-99%, continues to be a synthetic challenge. In putting together the carbon structures of triquinanes **1**,[1] **2**,[1b,2] **3**,[3] and **4**,[4] one frequently employed strategy involving annulation of the C ring onto the A-B bicyclic intermediates has been plagued by either the difficulty in controlling the stereochemistry of the C-ring

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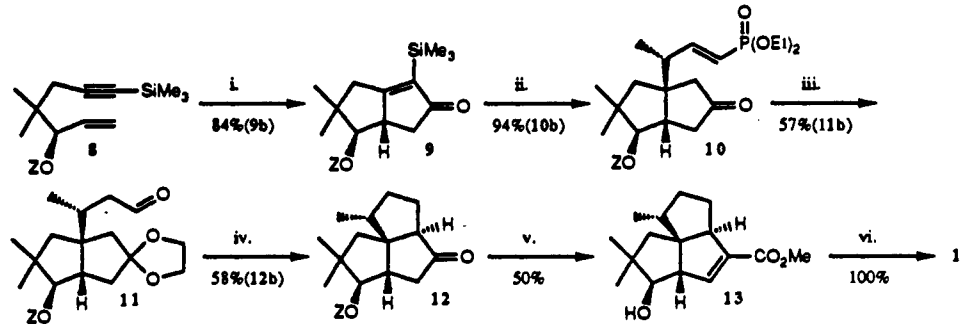
Scheme I[a]



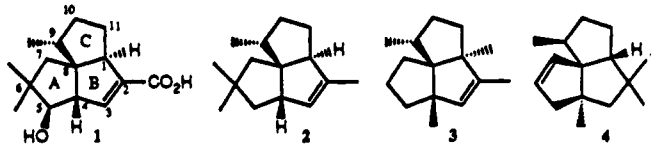
[a] **a**: Z = Bn. **b**: Z = MPM. (i) (1) *n*-BuLi (2.4 equiv), Cl_2ZrCp_2 (1.2 equiv), THF, −78 to 20 °C, overnight. (2) CO (1.1 atm), 3 h, −20 °C. (ii) (1) Diethyl (*Z*)-crotylphosphonate, *n*-BuLi, THF, −78 °C, 15 min. (2) $(n\text{-Bu})_4NF$, THF, 0 °C, 5 min. (iii) (1) $(CH_2OH)_2$, PPTS, benzene. (2) BH_3·THF, 20 °C, overnight, then 30% H_2O_2, NaOAc, 50 °C. (3) $NaHCO_3$, MeOH–H_2O, 50 °C, 3 h. (iv) (1) PPTS (1 equiv), acetone, H_2O reflux, 16 h. (2) MsCl, NEt_3, CH_2Cl_2, 0 °C, 10 min. (3) DBU, benzene, reflux, 10 min. (4) H_2, Pd/C, EtOAc, 20 °C, 10 h. (v) (1) LDA then Tf_2NPh, DME, −78 to 20 °C, 26 h. (2) CO (1.1 atm), $Pd(OAc)_2$, PPh_3, NEt_3, DMF, MeOH, 20 °C, 16 h. (3) DDQ, CH_2Cl_2, H_2O, 20 °C, 45 min. (vi) KOH, MeOH–H_2O, 45 °C, 3 h.

Table I. Preparation of Aldehydes via Hydroboration–Oxidation–Elimination of Alkenylphosphonates[a]

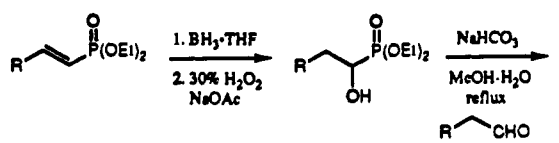
R of (*E*)-RCH=CHPO(OEt)$_2$	product yield, %	
	$RCH_2CH(OH)PO(OEt)_2$[b]	RCH_2CHO[c]
n-C_5H_{11}	97	98[d]
$PhCH_2$	85	65[d]
$PhCH_2CH_2$	95	80
e	92	85
f	95	*g*
h	92	76

[a] (*E*)-1-Alkenylphosphonates were treated for 16 h at 20 °C with 1 M borane in THF. After addition of aqueous NaOAc, 30% H_2O_2 was slowly added to the hydroboration mixture, and its temperature was maintained at 50 °C for 10–15 min. After extractive workup (aqueous NH_4Cl and ether), the crude product was treated with $NaHCO_3$ in refluxing MeOH–H_2O (1:1) for 1–3 h. [b] By ^1H NMR. [c] Isolated yield unless otherwise mentioned. [d] By GLC. [e] 1-(3-Oxocyclopentyl)ethyl. [f] An (*E*)-RCH=CHP(O)Ph_2 analogue of *e*. [g] No α elimination took place. [h] The ethylene ketal derivative of **10b**.

methyl group[2a,b] or the lack of regioselectivity in the C-ring annulation.[2c]

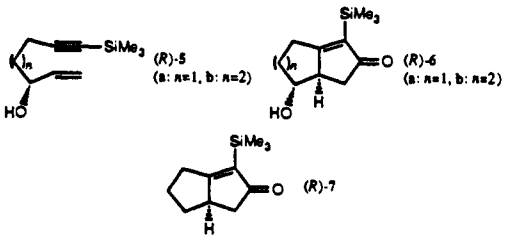


We now report here a highly selective method featuring (i) Zr-promoted diastereoselective (≥99%) enyne bicyclization–carbonylation and (ii) cyclopentannulation via allylphosphonate conjugate addition. Crucial to the development of the latter is the finding that hydroboration of vinylphosphonates with BH_3·THF is essentially 100% regioselective, producing, after oxidation, (α-hydroxyalkyl)phosphonates, which can be readily converted to the corresponding aldehydes (eq 1). To demonstrate the synthetic utility of this methodology, (±)-pentalenic acid[1] was prepared, as shown in Scheme I. Throughout the synthesis, essentially complete control of stereo- and/or regiochemistry was achieved.



(1)

We first sought a stereocontrolled route to bicyclic enones via Zr-promoted bicyclization–carbonylation[5] following promising leads in recent studies,[6] especially that obtained with enynes containing an allylic OH group.[6d,7] 3-Hydroxy-7-(trimethylsilyl)-1,6-heptenyne[6d] (**5a**) was subjected to the Sharpless kinetic resolution[8] using 1.5 equiv of *t*-BuOOH, 0.1 equiv of $Ti(OPr\text{-}i)_4$, 0.15 equiv of dicyclohexyl (+)-tartrate ((+)-DCHT), and molecular sieves (3 Å, 30 wt % of **5a**) in CH_2Cl_2 at −20 °C for 44 h to give (*R*)-**5a** (>98% ee) in 35% yield, the theoretical maximum being 50%. The Zr-promoted bicyclization–carbonylation of



(*R*)-**5a**, using 1.05 equiv of Cp_2ZrCl_2 in THF and 3.1 equiv of *n*-BuLi (−78 °C for 1 h and then 25 °C overnight) for bicyclization and 1.1 atm of CO (−30 °C for 5–10 h) for carbonylation, gave a 68% yield of **6a**, the enantiomeric purity of which was >98% by analysis of the ^1H and ^{13}C NMR spectra of its (+)-methoxy(trifluoromethyl)phenylacetic acid (MTPA) ester. The relative stereochemistry of the two adjacent chiral centers in **6a** was determined by ^1H 2D NOESY/COSY NMR spectrometry. Our preliminary results also indicate that removal of the OH group of **6a** to give spectroscopically homogeneous **7** can be achieved in 60% yield by treatment of **6** with phenyl chlorothionoformate and pyridine[9] followed by $(n\text{-Bu})_3SnH$ and 5% azobis(isobutyronitrile) (AIBN) in refluxing toluene. Similar results were obtained for conversion of **5b** into (*R*)-**5b** and **6b**.

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For the synthesis of pentalenic acid (1), enyne **8** was prepared in 78% overall yield by propargylation of ethyl isobutyrate, reduction with $LiAlH_4$, silylation, oxidation with $(COCl)_2$ and DMSO, and vinylation with vinylmagnesium bromide. After benzylation, Zr-promoted bicyclization–carbonylation[5] gave a 68% yield of **9a**, the stereochemistry of which was firmly established by NMR spectroscopy (J_{H^5,H^6} = 9.8 Hz) and X-ray analysis. For the eventual synthesis of **1**, it was necessary to use *p*-methoxybenzyl chloride[10] in place of benzyl chloride for protecting the OH group of **8** due to the difficulty in debenzylation. The bicyclization–carbonylation reaction for producing >98% diastereomerically pure **9b** proceeded in 84% yield.

For selective annulation of the C ring with control of the stereochemistry of the 9-Me group, **9b** was treated at −78 °C for 15 min with the lithio derivative of (Z)-$CH_3CH{=}CHCH_2PO(OEt)_2$[11] generated by its reaction with *n*-BuLi in THF at −78 °C. Crudely isolated conjugate addition product was treated with $(n\text{-Bu})_4NF$ (0 °C, 5 min) to give a 94% yield of **10b**, which was of ≥98% stereoisomeric purity. After ketalization of **10b** with $(CH_2OH)_2$, hydroboration with BH_3·THF[12] overnight at 20 °C followed by oxidation with 30% H_2O_2 and NaOAc at 50 °C yielded the corresponding (α-hydroxyalkyl)phosphonate, which was crudely isolated and treated with $NaHCO_3$ in MeOH–H_2O at 50 °C to give **11b** in 57% yield.[13] In addition to the conjugate addition of allylphosphonate anions, the base-promoted reaction of aldehydes with $CH_2[PO(OEt)_2]_2$ readily produces (E)-alkenylphosphonates in good yields,[14] typically 80–95%. Coupled with hydroboration–oxidation–elimination, one-carbon homologation of aldehydes can be achieved in good yield, as shown in Table I.

Treatment of **11b** with 1 equiv of pyridinium *p*-toluenesulfonate (PPTS) in boiling acetone–water for 16 h not only deprotected the carbonyl group but also induced aldolization in 82% yield. After mesylation with MsCl and NEt_3, treatment with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in refluxing benzene yielded the desired enone, which was hydrogenated over Pd/C to give isomerically pure **12b** in 71% yield based on the aldol intermediate. Conversion of **12b** into **13** using 2,6-di-*tert*-butyl-4-methylpyridine and triflic anhydride for generation of alkenyl triflates[1d] followed by Pd-catalyzed carbomethoxylation[15] led to a 75:25 mixture of **13** and its regioisomer. On the other hand, treatment of **12b** with lithium diisopropylamide (LDA) and Tf_2NPh in DME (dimethoxyethane) for triflate generation[16] followed by deprotection of the (*p*-methoxyphenyl)methyl (MPM) group with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) gave isomerically pure **13**, the spectra data of which were in excellent agreement with those obtained by other workers.[1] The Me ester **13** was quantitatively converted to (±)-**1** by hydrolysis with methanolic KOH.

Acknowledgment. We thank the National Institutes of Health (GM36792) and the National Science Foundation (CHE-9023728) for support of this research. We also thank Professors H. C. Brown, M. T. Crimmins, T. Hudlicky, and H. Seto for providing us with useful information and Dr. P. E. Fanwick and Mr. M. Piotto for spectral measurements.

Supplementary Material Available: Experimental procedures and analysis data for the compounds in this communication and an ORTEP view of **9a** (9 pages). Ordering information is given on any current masthead page.

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General Acid Catalysis of the Reduction of *p*-Benzoquinone by an NADH Analogue

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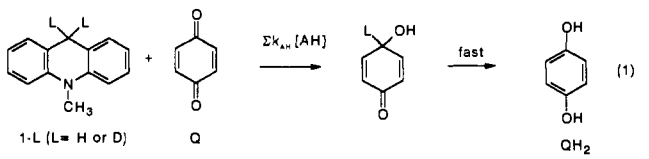
We report that the third-order term for acetic acid catalyzed reduction of *p*-benzoquinone, Q, by an NADH analogue, 9,10-dihydro-10-methylacridine (**1**-L, L = H or D; eq 1), displays primary isotope effects k_H/k_D = 1.5 in H_2O and D_2O and solvent isotope effects k_{H_2O}/k_{D_2O} = 1.3 for H or D transfer. Substituted RCOOH catalysts show a Brønsted slope α = 0.85. These results provide evidence for concerted hydron and hydride transfer to benzoquinone and are not consistent with a mechanism involving the semiquinone radical, QH•.[1]



Extensive studies of thermal 1,4-dihydronicotinamide reductions using isotope effects,[2] as well as kinetic and thermodynamic data,[3-6] have largely settled the question of whether the transfer of a hydride equivalent involves sequential one-electron transfers (e^-–H^+–e^-) or the transfer of a hydride ion in a single step.[7] In definitive cases where the e^-–H^+–e^- mechanism has been established, the electron acceptor has a one-electron reduction potential $E°$ > 0.4 V (NHE), much larger than that of most carbonyl compounds.[3,8-10] Nevertheless, the interaction of carbonyl compounds with Lewis acids may enhance their electron affinity[1,11] by stabilization of the developing substrate radical anion in a pathway that avoids the high-energy intermediates involved in either electron transfer to or Lewis acid complexation with the substrate.[15] Because such complexation is known to catalyze NADH-dependent reductions of the carbonyl group in enzyme[16] and non-enzyme[1,17,18] reactions, it is of interest to establish the

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