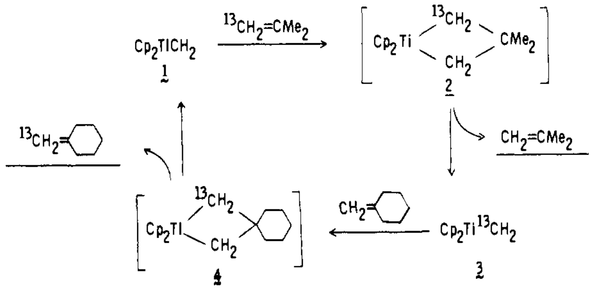
Scheme I. The ClAlMe$_2$ Group Is Omitted for Clarity. Each step is Considered Reversible



to metal and olefin methylene groups (eq 3). Since methylene hydrogen and methylene carbon equilibrations take place on

$$(C_5H_5)_2TiCD_2AlCl(CD_3)_2 + CH_2{=}CR_2 \rightleftharpoons (C_5H_5)_2TiCH_2AlCl(CD_3)_2 + CD_2{=}CR_2 \quad (3)$$

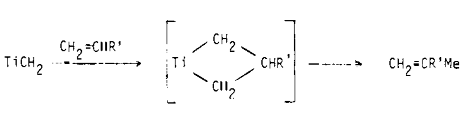
$$R_2 = (CH_3)_2 \text{ or } -CH_2(CH_2)_3CH_2-$$

the same time scale, it is likely that the CH$_2$ groups exchange as units. Methylenecyclohexane undergoes the analogous exchange reaction with (C$_5$H$_5$)$_2$TiCD$_2$AlCl(CD$_3$)$_2$ at approximately the same rate as isobutene.

In the metathesis experiment, a mixture of isobutene and methylenecyclohexane, supplied as ^{13}CH$_2$=CMe$_2$ (0.4 mmol) and CH$_2$=C$_6$H$_{10}$ (0.4 mmol), was combined with Cp$_2$TiCH$_2$AlClMe$_2$ (0.1 mmol) in benzene-d_6 solution (0.6 mL). Metathesis is indicated by the appearance of CH$_2$=CMe$_2$, ^{13}CH$_2$=C$_6$H$_{10}$, and Cp$_2$Ti^{13}CH$_2$AlClMe$_2$ and the disappearance of ^{13}CH$_2$=CMe$_2$, CH$_2$=C$_6$H$_{10}$, and Cp$_2$TiCH$_2$AlClMe$_2$. Reaction is extensive after 47 h at 51 °C and is limited to methylene group exchange (^{1}H NMR). Decomposition or byproduct formation are not detected under these conditions. This system thus performs the "degenerate"[7,8] olefin metathesis reaction with chemical and isotopic selectivity.

This degenerate metathesis is nicely explained by the mechanism of Scheme I, which is derived from the currently accepted mechanism for more typical olefin metatheses.[2] As in the conventional mechanism, a methylene complex **1** reacts with olefin (^{13}CH$_2$=CMe$_2$) to form a metallacyclobutane, **2**. Cleavage of the metallacycle in the proper sense yields a new olefin and a new metal alkylidene. With this mechanism, coordination of only one olefin at a time is required to produce exchange of alkylidene units between two olefins.

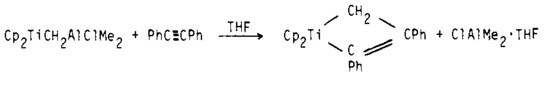
This scheme is thoroughly consistent with that proposed for homologation of ethylene and propylene.[1] With these olefins, which contain a hydrogen substituent at both ends of the double bond, the metallacycle **5** undergoes facile β-hydrogen transfer and olefin elimination before methylene exchange can occur (eq 4). Olefins of the type CH$_2$=CR$_2$ do not yield analogous products because they preferentially produce metallacycles with alkyl groups substituted in the β position (**2** and **4**, Scheme I).



(4)

5, R' = H or CH$_3$

Metallacyclobutanes thus seem plausible intermediates in the three known reactions of olefins with **1**, metathesis, homologation, and the cyclopropanation reported previously.[1] Although there is no direct evidence for the metallacyclobutane, we have isolated a metallacyclobutene (**6**) from the reaction of **1** with diphenylacetylene in tetrahydrofuran (THF)[9] (eq 5). The metallacyclobutene is probably more stable toward carbon-carbon bond breaking or coupling reactions than the related cyclobutanes because the formation of acetylenes or cyclopropenes is energetically less favorable.



(5)

6

The role of aluminum in these reactions is not yet clear. Aluminum coordinated to the methylene group in **1** is responsible for its long-term stability, and aluminum bonding may affect the interactions of **1** with CH$_2$=CR$_2$ in aromatic solvents.[1] This question will be explored further because compounds such as C$_2$H$_5$AlCl$_2$ are important for the activity of some of the best conventional olefin metathesis catalysts.

Acknowledgment. We thank D. K. Babcock for skilled experimental assistance.

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(2) For a recent review of olefin metathesis chemistry, see R. H. Grubbs, *Prog. Inorg. Chem.*, **24**, 1-50 (1978).

(3) Labeled isobutenes were purchased from Merck Sharp and Dohme, Canada, Ltd.

(4) After 8 days, the olefin was separated from the reaction mixture and was found by the mass spectrum to be isobutene, ^{12}C enriched. Isotopically normal isobutene was then charged to the ^{13}C-enriched organometallic. As the reaction mixture was heated overnight, metal and olefin methylene exchange occurred as expected.

(5) Trimethylaluminum-d_9, prepared from dimethylmercury-d_6 (Orgmet) and aluminum,[6] was reacted with Cp$_2$TiCl$_2$ to produce (C$_5$H$_5$)$_2$TiCD$_2$AlCl(CD$_3$)$_2$.

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(9) Synthesis, structure (R. L. Harlow), and chemistry of titanacyclobutenes will be reported separately.

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Pentamethylcyclopentadienyl Organoactinides. Trivalent Uranium Organometallic Chemistry and the Unusual Structure of Bis(pentamethylcyclopentadienyl)uranium Monochloride

Sir:

A conspicuous and important property of transition metal organometallic compounds is the tendency for the metal ions to exist in a number of formal oxidation states and to pass facilely between them. In contrast, the vast majority of organothorium and organouranium compounds contain the metal in the tetravalent oxidation state.[1,2] The known trivalent[3-5] compounds consist largely of triscyclopentadienyls, M(η^5-C$_5$H$_5$)$_3$,[3,4] and their Lewis base (L) adducts, M(η^5-C$_5$H$_5$)$_3$-L.[3,4] Owing to low solubility, what appears to be coordinative saturation, and nonroutine syntheses, the chemistry of these trivalent complexes has not been investigated in detail. Thus, there is very little known about the kinds of organometallic compounds which may exist for actinides in the +3 oxidation state and the reaction patterns which they undergo. In this communication we report that trivalent uranium, when complexed by the pentamethylcyclopentadienyl ligand,[6] possesses an extensive organometallic chemistry which includes, among

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other interesting features, metal-to-carbon and metal-to-nitrogen σ-bond formation, Lewis base adduct formation, and ligand reductive coupling. We also report the unusual molecular structure of the precursor for these studies, trimeric bis(pentamethylcyclopentadienyl)uranium(III) chloride, $\{U[\eta^5\text{-}(CH_3)_5C_5]_2Cl\}_3$.

Bis(pentamethylcyclopentadienyl)uranium chloride (**1**) can be synthesized by any of four procedures. Hydrogenolysis of the known, tetravalent, uranium alkyl chlorides[6a,d] quantitatively precipitates **1** as dark green, air-sensitive crystals:

$$3U[(CH_3)_5C_5]_2(R)Cl + \tfrac{3}{2}H_2\ (1\ \text{atm}) \xrightarrow[25\ °C]{\text{toluene}} \underset{\mathbf{1}}{\{U[(CH_3)_5C_5]_2Cl\}_3} + 3RH \qquad (1)$$

$$R = CH_3,\ CH_2Si(CH_3)_3$$

This reaction presumably proceeds via the unstable uranium chlorohydride, $\{U[(CH_3)_5C_5]_2(H)Cl\}_2$. Support for this intermediate is derived from the observation that the analogous reaction for thorium (IV), which is only reduced with great difficulty,[1a,3,7] yields the stable species $\{Th[(CH_3)_5C_5]_2(H)Cl\}_2$.[8] Alternatively, **1** may be prepared by two other procedures

$$3U[(CH_3)_5C_5]_2Cl_2 + 3Li(t\text{-}C_4H_9) \xrightarrow[-78\ °C]{\text{ether}} \mathbf{1} + 3LiCl + \text{organic products} \qquad (2)$$

$$\tfrac{3}{2}\{U[(CH_3)_5C_5]_2H_2\}_2 + 3U[(CH_3)_5C_5]_2Cl_2 \rightarrow 2(\mathbf{1}) + 3H_2 \qquad (3)$$

which also probably involve the unstable chlorohydride (via β-hydride elimination[3c,9] within the chloro *tert*-butyl derivative or by hydride-halide interchange with the known dihydride) as well as by sodium amalgam reduction of the dichloride:

$$U[(CH_3)_5C_5]_2Cl_2 \xrightarrow[\text{toluene}]{Na/Hg} \mathbf{1} + NaCl \qquad (4)$$

The monochloride was characterized by standard analytical techniques;[10] it is insufficiently soluble in noncoordinating solvents for molecular weight determination.

Single crystals of **1**, obtained by allowing a toluene solution of $U[(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$ to stand under an atmosphere of dihydrogen, are monoclinic, space group $C2/c\text{-}C_{2h}^6$ (No. 15) with $a = 21.886$ (7), $b = 14.236$ (5), $c = 24.517$ (7) Å; $\beta = 128.65$ (2)°; and $Z = 4$ (trimeric species). Three-dimensional diffraction data (a total of 10 891 independent reflections having $2\theta_{\mathrm{Mo}\ K\bar{\alpha}} < 65.2°$) were collected on a computer-controlled Syntex $P\bar{1}$ autodiffractometer using graphite-monochromated Mo $K\bar{\alpha}$ radiation and full (1° wide) ω scans. The structural parameters have been refined to convergence (R (unweighted, based on F) = 0.069 for 2922 independent reflections having $2\theta_{\mathrm{Mo}\ K\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$) in cycles of unit-weighted full-matrix least-squares refinement which used anisotropic thermal parameters for all nonhydrogen atoms.[11]

The structural analysis shows that crystals of **1** are composed of discrete trinuclear $[(\eta^5\text{-}(CH_3)_5C_5)U(\mu_2\text{-}Cl)]_3$ molecules (Figure 1) in which each U(III) ion adopts the familiar pseudotetrahedral "bent sandwich" $M(\eta^5\text{-}C_5H_5)_2X_2$ configuration.[5b,12] The X groups are doubly bridging Cl^- ligands which serve to generate the planar (to within 0.02 Å) six-atom (-U-Cl-)$_3$ ring. Thus, the structure is similar to that of $[Zr(\eta^5\text{-}C_5H_5)_2O]_3$,[13a] but differs from that of dimeric $[Bk(\eta^5\text{-}C_5H_5)_2Cl]_2$.[13b] Although the molecule is required crystallographically to possess only C_2 symmetry (with the C_2 axis passing through U_A and Cl_2 of Figure 1), it approximates rather closely D_{3h} symmetry with the idealized threefold axis being oriented perpendicular to the (-U-Cl-)$_3$ grouping and passing through its center of gravity. Each of the five-membered rings for the pentahapto-bonded pentamethylcyclopentadienyl ligands are coplanar to within 0.02 Å and their least-squares mean planes intersect that of the (-U-Cl-)$_3$ ring in dihedral angles of 19.7-28.6°. Least-squares mean planes for each U and the Cl opposite it in the (-U-Cl-)$_3$ ring as well as the centers of gravity (C_g) for its two cyclopentadienyl rings intersect that of the (-U-Cl-)$_3$ grouping in dihedral angles of 81.7-86.0°.

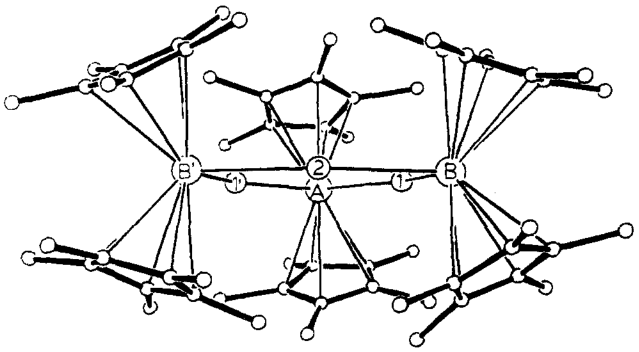


Figure 1. Perspective drawing (adapted from an ORTEP plot) of the $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$ molecule (**1**). Uranium and chlorine atoms are represented by large- and medium-sized open circles labeled with capital letters and numbers, respectively. Carbon atoms are represented by small open circles and all hydrogen atoms are omitted. Atoms labeled with a prime (′) are related to those labeled without a prime by the crystallographic C_2 axis which passes through U_A and Cl_2.

Bond lengths and angles for selected chemically distinct bonds in **1**, averaged according to approximate D_{3h} symmetry, are as follows: U-C, 2.76 (3, 3, 9, 15),[14] U-Cl, 2.901 (5, 10, 16, 3), U··U, 5.669 (2, 10, 15, 3), C-C (cyclopentadienyl ring), 1.40 (4, 2, 7, 15), C-C (Cp ring to methyl), 1.53 (4, 2, 5, 15), U-C_g, 2.48 (-, 1, 2, 3) Å; Cl-U-Cl, 84.5 (3, 16, 24, 3)[14], C_g-U-C_g, 127.9 (-, 5, 7, 3), C_g-U-Cl, 109.0 (-, 37, 60, 6), U-Cl-U, 155.5 (4, 27, 31, 3)°.

Although **1** is insoluble in hydrocarbon solvents, it readily dissolves in the presence of Lewis base donors to form the corresponding adducts:

$$\mathbf{1} + 3xL \rightleftharpoons 3U[(CH_3)_5C_5]_2Cl\cdot xL \qquad (5)$$

L = pyridine, x = 1 (blue-black needles)
L = THF, x = 1 (green needles)
L = diethyl ether (green needles)
L = $P(CH_3)_3$ (green needles)

The pyridine and THF adducts are sufficiently stable to allow isolation and drying in vacuo.[15a] The diethyl ether complex is somewhat less stable, and the trimethylphosphine complex rapidly decomposes under vacuum.[16] The ^1H NMR spectra of these adducts are characterized by an isotropically shifted[17] pentamethylcyclopentadienyl CH_3 resonance in the region δ ca. −5 (line width (lw) ≈ 40-100 Hz).[18a] The resonances of the Lewis bases are also broadened and shifted;[18a] addition of excess base evidences rapid exchange of the free and coordinated molecules.[18b] These and the results below (vide infra) represent the first NMR data on well-defined U(III) organometallics.[1a,17]

Alkylation of **1** with the sterically bulky lithium reagent, $LiCH[Si(CH_3)_3]_2$,[20a] yields a thermally stable, monomeric uranium(III) alkyl complex (**2**):

$$\tfrac{1}{3}(\mathbf{1}) + LiCH[Si(CH_3)_3]_2 \xrightarrow[25\ °C]{\text{ether}} \underset{\mathbf{2}}{U[(CH_3)_5C_5]_2CH[Si(CH_3)_3]_2} + LiCl \qquad (6)$$

This compound was obtained on recrystallization from pentane as black needles, which were characterized by the usual techniques.[19] The ^1H NMR of **2** displays isotropically shifted resonances at δ −5.26 (30 H, s, lw = 19 Hz) and −22.8 (18 H, s, lw = 20 Hz) which are assigned to ring and alkyl group methyl resonances, respectively. The methine proton resonance could not be located. Interestingly, the use of less bulky alkyl groups leads to thermally unstable products; a similar effect has been observed in biscyclopentadienyltitanium(III) chemistry[20] and appears to reflect the tendency of the bulky alkyl to hinder various intra- and/or intermolecular decomposition processes.[9a] As found for the uranium(IV) alkyls,[6d] the uranium(III) alkyl undergoes rapid hydrogenolysis to generate the known, tetravalent uranium dihydride:[6d]

$$2(\mathbf{2}) + 3H_2 \xrightarrow[25\ °C,\ 10\ min]{toluene} \{U[(CH_3)_5C_5]_2H_2\}_2 + 2CH_2[Si(CH_3)_3]_2 \quad (7)$$

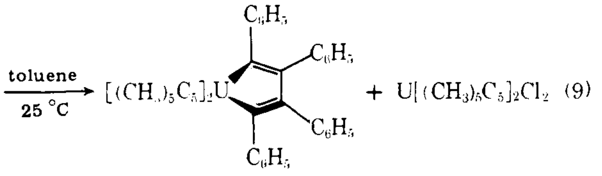
In a reaction similar to eq 6, it was also possible to prepare an organouranium(III) amide **3**.[21]

$$\tfrac{1}{3}(\mathbf{1}) + NaN[Si(CH_3)_3]_2 \xrightarrow[25\ °C]{ether} \underset{\mathbf{3}}{U[(CH_3)_5C_5]_2N(Si(CH_3)_3)_2} + NaCl \quad (8)$$

This compound was crystallized from toluene–pentane as blue-black needles and was characterized by standard methods.[22]

The reaction of **1** with excess diphenylacetylene leads to reductive coupling of the alkyne. Produced in this interesting "disproportionation" reaction are the known uranium(IV) metallocycle (**4**)[6a,d] and the uranium(IV) dichloride[6d] in quantitative yield (eq 9). Here the trimer formally donates 1.5 equiv of "U[(CH$_3$)$_5$C$_5$]$_2$", which in turn reduces and couples two acetylene moieties. Such reductive coupling reactions have been previously observed for low-valent transition metals,[23] but not for actinides.

$\tfrac{2}{3}(\mathbf{1}) + 2C_6H_5C{\equiv}CC_6H_5$



4

The results of this study indicate a rich and diverse organometallic chemistry for trivalent uranium. As noted for the tetravalent actinides,[6] there is again a distinct similarity to early transition metal organometallic chemistry. The relationship of this U(III) chemistry to that of other low-valent f-element ions, as well as to that of d-element ions, is under continuing investigation.

Acknowledgments. We thank the National Science Foundation (T.J.M., CHE76-84494 A01) and the University of Nebraska Computing Center (V.W.D.) for generous support of this work.

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(10) This compound exhibits infrared transitions (Nujol mull) at 1019 (m) and 799 (m) cm^{-1} which are characteristic of an η^5-(CH$_3$)$_5$C$_5$ ligand.[6,8] Anal. Calcd for C$_{60}$H$_{90}$U$_3$Cl$_3$: C, 44.16; H, 5.56; Cl, 6.52. Found: C, 44.09; H, 5.59; Cl, 6.60.

(11) Refinement is continuing with the more complete ($2\theta_{Mo\ K\bar{\alpha}} < 65.2°$) data set.

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(14) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

(15) (a) Besides infrared transitions (Nujol mulls) due to the η^5-(CH$_3$)$_5$C$_5$ ligand at 1019 (m) and 799 (w) cm^{-1}, these complexes exhibit absorptions at 1591 (m), 1482 (m), 1438 (s), 1210 (m), 1060 (m), 1037 (m), 1001 (m), 750 (s), 700 (s), and 621 (m) (pyridine) and 1032 (s), 916 (m), and 898 (m) (THF) cm^{-1} which are characteristic of the coordinated bases.[15b–d] Anal. Calcd for C$_{24}$H$_{38}$ClOU: C, 46.79; H, 6.22; Cl, 5.75. Found, C, 46.71; H, 6.18; Cl, 5.75. Anal. Calcd for C$_{25}$H$_{35}$ClNU: C, 48.20; H, 5.66; N, 2.25; Cl, 5.69. Found: C, 48.16; H, 5.70; N, 2.31; Cl, 5.63. (b) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; pp 211–212. (c) Bellamy, L. J. "The Infra-red Spectra of Complex Molecules", 3rd ed.; Chapman and Hall: London, 1975; pp 311–314, 130–135. (d) Marks, T. J.; Grynkewich, G. W. *Inorg. Chem.* **1976**, *15*, 1302–1307.

(16) Loss of base was accompanied by visible crumbling of the crystals in the case of the diethyl ether and trimethylphosphine derivatives. The value of x (eq 5) could not be determined with certainty for the ether and trimethylphosphine complexes.

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(18) (a) The pyridine adduct displays ^{1}H NMR resonances at δ −4.95 (30 H, lw = 40 Hz, CH$_3$), −56.6 (2 H, lw = 75 Hz, pyridine), −9.19 (2 H, lw = 14 Hz, pyridine), 7.02 (1 H, lw = 8 Hz, pyridine), while the THF adduct displays resonances at δ −4.86 (30 H, lw = 100 Hz, CH$_3$), −14.3 (4 H, lw = 120 Hz, THF), and −47.6 (4 H, lw = 180 Hz, THF). (b) Incremental addition of free base produces a single set of base resonances which progressively shift toward the diamagnetic position. The resonance frequency and line width of the η^5-(CH$_3$)$_5$C$_5$ signal remains essentially unchanged throughout this process.

(19) The infrared spectrum of **2** exhibits absorptions at (Nujol mull): 1250 (s), 1239 (s), 1019 (m), 858 (s), 829 (s), 756 (m), and 574 (m) cm^{-1}. Anal. Calcd for C$_{24}$H$_{49}$Si$_2$U: C, 48.56; H, 7.39; mol wt, 668 g/mol. Found: C, 48.44; H, 7.31; mol wt, 623 ± 10% g/mol (cryoscopic in benzene).

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(22) The infrared spectrum of **3** has absorptions at (Nujol mull) 1255 (m), 1242 (s), 1025 (s), 862 (s), 833 (s), 820 (s), 760 (m), 590 (m) cm^{-1}; ^{1}H NMR exhibits resonances at δ −5.43 (30 H, singlet, lw = 7 Hz, CH$_3$), −24.9 (18 H, s, lw = 20 Hz, CH$_3$). Anal. Calcd for C$_{27}$H$_{49}$NSi$_2$U: C, 46.69; H, 7.23; N, 2.09; mol wt, 676. Found: C, 46.77, H, 7.19; N, 2.27; mol wt, 668 ± 10% (cryoscopic in benzene).

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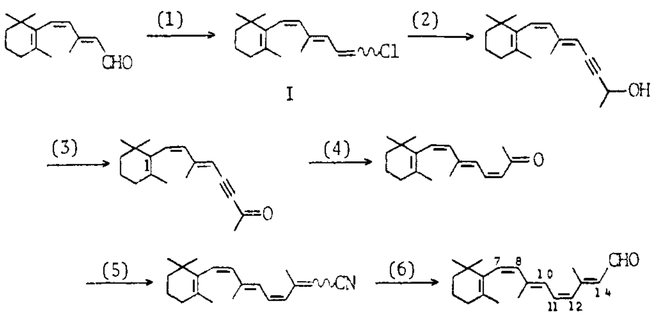
Doubly Hindered 7,11-Dicis Isomers of Retinal. Synthesis, Properties, and Interaction with Cattle Opsin[1]

Sir:

With the preparation of four geometric isomers of vitamin A containing the hindered 7-cis geometry,[2] only 6 of the possible 16 isomers are still unknown. Among these are the 4 containing the doubly hindered 7,11-dicis geometry (7,11-dicis, 7,9,11-tricis, 7,11,13-tricis, and all-cis).[3] Considering the relative instability of isomers containing either the 7-cis or the 11-cis geometry, one might reasonably question the possible existence of the doubly hindered isomers. In this paper we report preliminary results on studies of such isomers.

The pathway that led to successful synthesis of 7,11-*cis*^{2}-retinal is shown in Scheme I.

Scheme I^{a}



^{a}(1) Ph_3PCH_2ClBr, *n*-BuLi; (2) 2 mol equiv of *n*-BuLi, CH_3CHO; (3) MnO_2; (4) H_2/Lindlar; (5) $(EtO)_2POCH_2CN$–NaH; (6) Dibah.

The starting triene was prepared according to the procedure reported earlier.[4] It was separated from the 7,9-dicis isomer by repeated passage through two silica gel columns on a Waters Prep-500 HPLC unit. Most of the reactions are adapted from those already in the literature for the synthesis of the 7-trans isomers.[5] All steps resulted in yields >50%. We might comment that step 4 of the sequence (hydrogenation over Lindlar catalyst) proceeded cleanly with no side reactions. Reaction 5 when conducted in benzene–DMF mixture (15:1) resulted in high trans stereoselectivity of the newly formed 13,14 double bond (>90%). The major isomer was readily purified on a silica gel column. Partial reduction with diisobutylaluminum hydride gave 95% yield of 7,11-*cis*^{2}-retinal.[6] The geometry of the new retinal isomer was characterized by its ^{1}H NMR data: $J_{7,8}$ = 12.0 and $J_{11,12}$ = 11.3 Hz (both cis geometry).[7] The complete spectrum is shown in Figure 1.

A slight modification of Scheme I led to a mixture containing predominantly 7,13-*cis*^{2}-11,12-dehydroretinal (II) (Scheme II). The preference for 13-cis isomer in cases involving adjacent triple bonds is well documented.[8] Hydrogenation over Lindlar catalyst, however, gave a rather complex mixture of which we only succeeded in isolating one identifiable product: 7,13-*cis*^{2}-retinal.[9] We suspect that it was formed by way of 7,11,13-*cis*^{3}-retinal involving two consecutive steps of 6e electrocyclization in a manner suggested by Kluge and Lillya.[10] This result suggests that this tricis and other unknown isomers of retinal containing the 11,13-dicis geometry (9,11,13-tricis and all-cis) are probably not stable at room temperature. A certainly related observation is the reported thermal instability of 11,13-*cis*^{2}-retinal.[11a] The isomer crystallized from a solution of purified 11,13-*cis*^{2}-retinal was in fact reassigned with the 13-cis geometry.[11b]

The UV absorption spectrum of 7,11-*cis*^{2}-retinal along with those of 7-cis, 11-cis, and all-trans isomers is shown in Figure 2. It is clear that the characteristic cis band in 11-*cis*-retinal is retained in the dicis isomer and at the same time the extinction coefficient of the main band is much lower presumably owing to nonplanarity of the polyene chain as a result of the doubly hindered geometry.

7,11-*cis*^{2}-Retinal, when incubated with cattle opsin in a manner similar to the procedures used in studies of other retinal isomers,[12] was found to form a stable pigment analogue at a

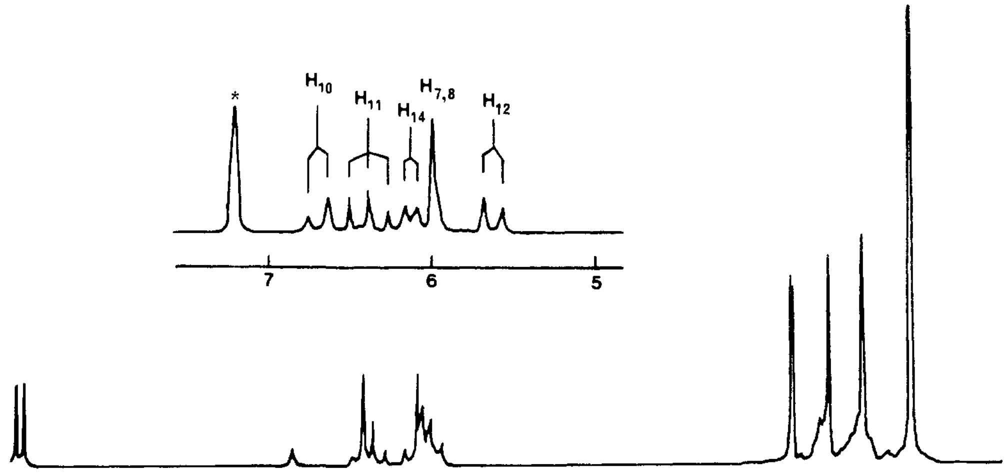


Figure 1. ^{1}H NMR spectrum (Varian XL-100) of 7,11-cis^{2}-retinal in CCl_4 (containing 5% of C_6D_6 for locking). Insert: expanded vinyl region of the same compound taken in C_6D_6. The peaks marked with * are due to isotopic impurities of solvent.

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