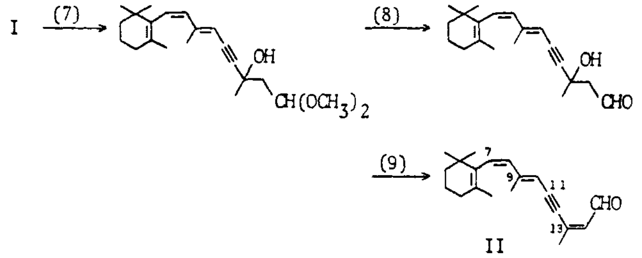
Scheme II[a]



[a] (7) 2 mol equiv of *n*-BuLi, $CH_3COCH_2CH(OCH_3)_2$; (8) *p*-TsOH·H_2O–acetone; (9) $CH_3SO_2Cl–Et_3N$, CH_2Cl_2.

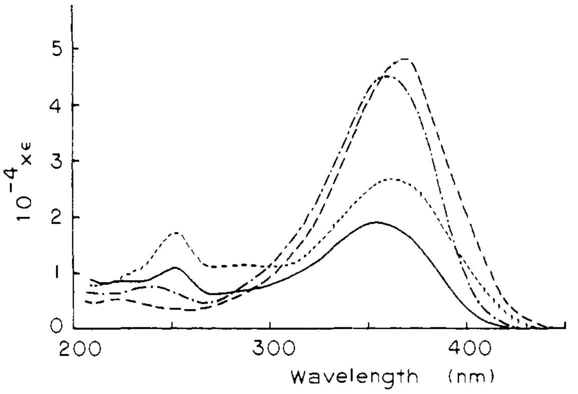


Figure 2. Absorption spectrum of 7,11-*cis*²-retinal in hexane (—) along with those of all-trans (- - -), 7-cis (-·-), and 11-cis (- - -). Data of all-trans and 7-cis (in heptane) were taken from ref 13. Data of 11-cis were obtained for this work but are essentially identical with those reported in ref 11: 7,11-dicis, λ_{max} 355 nm (ϵ 18 800); all-trans, 368 (48 000); 7-cis, 359 (44 100); 11-cis, 363 (26 400).

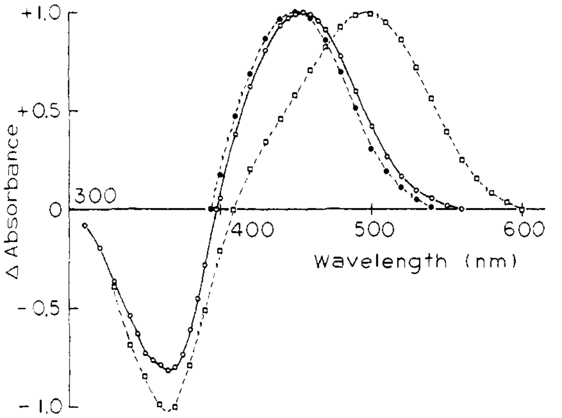


Figure 3. The normalized difference spectrum of digitonin solutions of 7,11-*cis*²-rhodopsin (—O) along with those of rhodopsin (- -□) and 7-*cis*-rhodopsin (- -●), obtained by subtracting the spectrum of the bleached from those of the unbleached pigment in the presence of 92 mM hydroxylamine. The data of rhodopsin and 7-*cis*-rhodopsin were obtained in our laboratory but are identical with those reported in ref 11 and 13.

rate ($k_2 \approx 1 \times 10^{-2}$ M^{-1} s^{-1}, in 2% digitonin dissolved in 10 mM Hepes buffer (pH 7.0) at 25 °C) considerably slower than that of 11-*cis*-retinal but comparable with those of the 7-cis,11-trans isomers.[13] The pigment is moderately stable in an excess of hydroxylamine. The difference spectrum of the pigment is shown in Figure 3 along with those of 7-*cis*-rhodopsin and rhodopsin. The absorption maximum is at 455 nm, only slightly red shifted from that of 7-*cis*-rhodopsin (450 nm). Although we have yet done the detailed experiment exploring properties of this new pigment analogue, in a preliminary experiment we showed that the pigment is bleachable by yellow light (≥450 nm). Experiments are underway to examine this photobleaching process. The question whether it takes place by one-photon two-bond isomerization[14] or via intermediacy of rhodopsin and 7-*cis*-rhodopsin is most intriguing.

Acknowledgment. The work was supported by grants from the U.S. Public Health Services (AM-17806, CP-75933). We thank Hoffmann-La Roche Co. for continued support in the form of generous supply of vitamin A related compounds.

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(8) See p 273, ref 5
(9) ^1H NMR ($CDCl_3$): 1.06, 1.54, 1.94, 2.10 (methyls), 5.98 (H_7), 6.11 (H_8), 6.36 (H_{10}), 6.92 (H_{11}), 7.22 (H_{12}), 5.80 (H_{14}), 10.10 ppm (H_{15}) ($J_{7,8}$ = 11.5, $J_{11,12}$ = 15.5 Hz). 7,13-*cis*²-Retinal was previously isolated as a mixture with 7,9,13-*cis*³-retinal (see ref 2).
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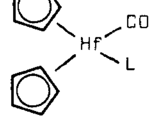
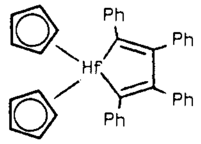
Structure and Reactivity of the First Hafnium Carbonyl, $(\eta^5\text{-}C_5H_5)_2Hf(CO)_2$

Sir:

In contrast to the rich and varied chemistry displayed by the more abundant members of group 4b, titanium and zirconium, the organometallic chemistry of hafnium has only recently begun to develop.[1] Earlier joint studies in our laboratories have been concerned with the formation, structure, and reactivity of compounds containing organohafnium σ bonds[2] and with hafnium-containing metallocycles.[3] We now report on the crystal and molecular structure of the first hafnium carbonyl, $(\eta^5\text{-}C_5H_5)_2Hf(CO)_2$ (**1**),[4,5] as well as on some thermally and photochemically induced reactions of this compound.



1 L = CO
2 L = PPh_3
3 L = PMe_3
4 L = $Ph_2PCH_2CH_2PPh_2$
5 L = PF_3



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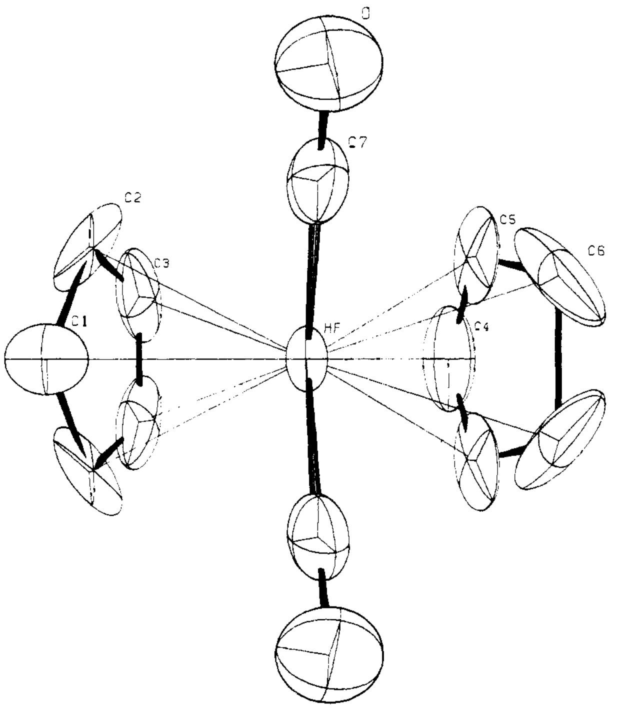

Figure 1. Molecular structure of $Cp_2Hf(CO)_2$, shown with 50% probability thermal ellipsoids. Other important bond lengths follow: Hf-Cent(1) = 2.15, Hf-Cent(2) = 2.17, C(7)-O = 1.14 (2) Å. Angles included the following: Hf-C(7)-O = 178 (1), C(7)-Hf-C(7)′ = 89.3 (9), Cent(1)-Hf-Cent(2) = 141, Cent(1)-Hf-C(7) = 103, Cent(2)-Hf-C(7) = 104°.

Crystals of **1** suitable for the X-ray diffraction study were grown by the slow cooling of a heptane solution at −20 °C. A purple crystal of the compound was sealed in a thin-walled glass capillary. The space group is $P2_1/m$, and the unit cell parameters are a = 6.497 (4), b = 11.411 (6), c = 8.072 (4) Å; β = 113.85 (5)°; and ρ_{calcd} = 2.21 g cm^{-3} for Z = 2. Least-squares refinement based on 982 observed reflections produced a final agreement index of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.059$. Hydrogen atoms were included and all nonhydrogen atoms were refined with anisotropic thermal parameters.

The molecule (Figure 1) resides on a crystallographic mirror plane which passes through both cyclopentadienyl rings and bisects the C(carbonyl)-Hf-C(carbonyl) bond angle. $(\eta^5\text{-}C_5H_5)_2Hf(CO)_2$ is not isostructural with its titanium analogue and the two molecules themselves exhibit a fundamental difference: in the former the cyclopentadienyl rings are staggered, while in the latter they are eclipsed. The Hf-C(carbonyl) bond distance, 2.16 (2) Å, agrees well with the predicted value of ~2.15 Å based on the 2.030 (11) Å Ti-C(carbonyl) length found in $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$[6] and the difference in metallic radii ($\Delta = r_{Hf} - r_{Ti}$ = 0.12 Å).[7]

In the structure of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$, the average Ti-C(cyclopentadienyl) distance, 2.35 (1) Å, is significantly shorter than that normally found for Ti-C(cyclopentadienyl) bonds in Ti^{4+} complexes. This was taken as evidence that the d^2 electrons occupy an orbital that is bonding with respect to the ring. The same effect is noted in $(\eta^5\text{-}C_5H_5)_2Hf(CO)_2$. Although the range is wide, 2.41 (2) to 2.55 (2) Å, the average, 2.45 (5) Å, is less than the typical value for Hf^{4+} complexes (2.482 (4) Å in $[(\eta^5\text{-}C_5H_4)_2(CH_2)_3]HfCl_2$).[8,9]

We find that all three group 4b metallocene dicarbonyls (M = Ti, Zr, Hf) readily undergo photochemically induced substitution reactions, the zirconium and hafnium derivatives being significantly more photolabile than the titanium analogue.[10] For example, photolysis of **1** and triphenylphosphine (10% molar excess) in heptane solution at 10 °C results in the facile displacement of a carbonyl ligand over a 4-h period, and subsequent formation of $(\eta^5\text{-}C_5H_5)_2Hf(CO)(PPh_3)$ (**2**) in moderate yield. Phosphine complex **2** was characterized by spectroscopic techniques and by a suitable elemental analysis. The ^1H NMR spectrum of **2** (C_6D_6, referenced to external Me_4Si) exhibits a doublet (J_{H-P} = 1.8 Hz) at τ 5.25 and a multiplet at 2.67–3.05, assignable to the cyclopentadienyl and the aromatic protons, respectively. The IR spectrum (THF) contains a single strong metal carbonyl absorption at 1830 cm^{-1}. By contrast, **1** appears to be unreactive toward triphenylphosphine in refluxing toluene for a 21-h period. In a similar manner, a photochemical reaction between **1** and excess trimethylphosphine has afforded an analogous monophosphine, $(\eta^5\text{-}C_5H_5)_2Hf(CO)(PMe_3)$ (**3**): NMR τ 5.17 (d, J_{H-P} = 2.0 Hz, $\eta^5\text{-}C_5H_5$), 9.10 (d, J_{H-P} = 6.5 Hz P-CH_3); IR ν_{CO} 1824 cm^{-1}. Attempts to substitute both carbonyl ligands in **1** with a chelating diphosphine, bis(1,2-diphenylphosphino)ethane (Diphos), under photochemical conditions, have thus far led only to a monosubstituted derivative (**4**): NMR τ 5.25 (d, J_{H-P} = 1.8 Hz, $\eta^5\text{-}C_5H_5$), 2.40–3.15 (m, Ph); IR ν_{CO} 1827 cm^{-1}.

Photolysis of **1** in heptane solution at 10 °C in the presence of excess PF_3 likewise gives $(\eta^5\text{-}C_5H_5)Hf(CO)(PF_3)$ (**5**) (NMR τ 5.21 (d, J_{H-P} = 2.5 Hz, $\eta^5\text{-}C_5H_5$); IR ν_{CO} 1910 cm^{-1}) together with unreacted **1**.[11] This reaction can also be conducted under nonphotochemical conditions at room temperature over a period of several days, in marked contrast to the reaction of **1** and triphenylphosphine. The higher energy carbonyl stretching frequency exhibited by **5** compared with that of monophosphine complexes **2–4** is in accord with the enhanced π-acceptor abilities of the PF_3 ligand.[13] It should also be noted that **2–5** represent the first hafnocene-phosphine complexes yet reported.

In view of the current widespread interest in reactions of metal carbonyls and acetylenes, **1** was photolyzed in benzene solution in the presence of 2 equiv of diphenylacetylene. The sole organometallic product (51%) was bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylhafnole (**6**): NMR τ 4.03 (s, $\eta^5\text{-}C_5H_5$), 2.85–3.40 (m, Ph); MS m/e 666 (M^+). The product can also be obtained in good yield by heating **1** and diphenylacetylene in refluxing toluene for a 24-h period. These procedures thus represent a convenient alternative route to hafnocycle **6**, which has previously been prepared only by the photolysis of dimethylhafnocene and diphenylacetylene.[14]

In view of the above results, it is apparent that **1** as well as its zirconium analogue $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$[15] can undergo a variety of photochemically and thermally induced reactions in the presence of various ligands, leading to organometallic compounds of both chemical and structural interest. Additional joint studies along these lines are in progress.

Acknowledgments. The authors are grateful to the National Science Foundation for support of this research program.

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(11) In all photochemical reactions involving **1** in heptane solution either alone or in the presence of phosphines, a yellow precipitate is also invariably formed. An IR spectrum (Nujol) of this product exhibits characteristic cyclopentadienyl bands as well as a strong absorption at 2055 cm^{-1}. The ^1H NMR spectrum (C_6D_6) of the yellow solid contains a single broad resonance centered at ca. τ 3.8 and is reminiscent of the spectrum of photochemically generated black titanocene.[12] The product, which may possibly be an oligomeric hafnocene carbonyl, is under further investigation.

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(15) All of the above reactions involving **1** have also been successfully completed for (η^5-$C_5H_5)_2Zr(CO)_2$: Sikora, D. J.; Rausch, M. D., unpublished studies.

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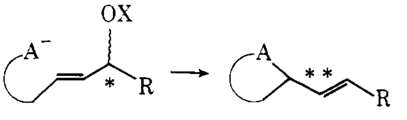
Concerted Intramolecular Displacement with Rearrangement in Allylic Systems. Displacement of an Allylic Ester with a Carbanion

Sir:

The formation of a ring by intramolecular displacement with rearrangement of an allylic departing group,[1] as shown in **1** → **2**, could be a valuable reaction:[2] if the displacement is stereospecific it will result in predictable transfer of chirality from the secondary alcohol center in **1** (easily obtainable from any readily available chiral ethynyl carbinol)[3] to a carbon atom of the newly formed ring.

Our initial investigation[1] of such an intramolecular internal $S_{N'}$ reaction (for which we suggest the symbol $S_{cN'}$[4]) represented by **1** → **2** showed that, when A is sulfur, reaction results in a transfer of chirality (* → **) which corresponds to very largely anti relationship of A^- and X in the transition state for the cyclization (to a tetrahydrothiophene).



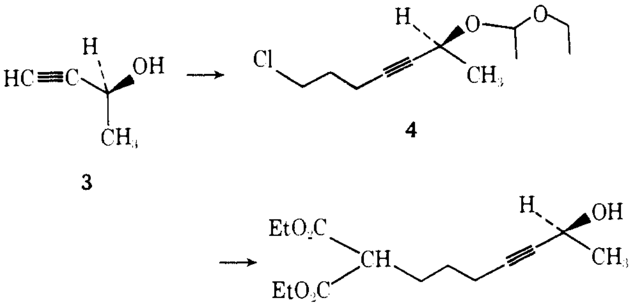
1 **2**

This result was surprising because it is in contrast to the clean syn relationship reported for the only previous cyclization of this type.[2a,5] In that instance, the departing oxygen function was part of an epoxide rather than, in our case, of an ester group; and the displacing group A was carbon rather than sulfur.

The difference in stereochemical course might be the result, inter alia, of different geometry relating entering and departing groups (metal chelation with epoxide?); or it might be due to some peculiarity of the sulfide ion (one-electron transfer?) involved in the cyclization in which A is sulfur.

In order to examine the latter possibility, as well as to establish the usefulness of the chiral synthesis shown in **1** → **2**, we have now examined the situation in which A in structure **1** above is carbon rather than sulfur and now demonstrate that anti relationship between entering and departing group is observed here also, resulting now in the formation of a cyclopentane ring.

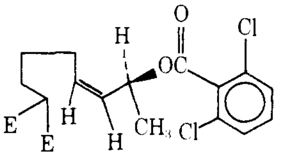
The required material for the cyclization studies was prepared starting with partially resolved (*S*)-(−)-1-butyn-3-ol[6] (**3**), $[\alpha]^{22}_D$ − 26.7° (*c* 3.3, dioxane), which had 49.7% enantiomeric excess.[7] Protection of the secondary hydroxyl group (ethyl vinyl ether, trace of $POCl_3$, 0–10 °C, 2 h), followed by alkylation with 1-bromo-3-chloropropane (1.5 equiv of $LiNH_2$–liquid NH_3, −33 °C, 8 h), gave the 1-ethoxyethyl ether of 7-chloro-3-heptyn-2-ol (**4**), bp 91–92 °C (0.35 mm).



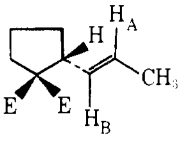
3 **4** **5**

Alkylation in the presence of sodium iodide (~0.3 equiv) with sodium diethylmalonate (~2 equiv of 1:3 DMF–EtOH, 105 °C, 12 h), followed by removal of the protecting group (~3:1:1 AcOH–THF–H_2O, 35 °C, 6 h), gave the ethynylcarbinol **5** which had $[\alpha]^{22}_D$ − 7.8 ° (*c* 1.95, benzene), after purification by MPLC on silica gel (30:70 ethyl acetate–hexane).[8] Selective hydrogenation (5% $Pd/BaSO_4$, CH_3OH, trace of quinoline) to the cis olefinic carbinol and esterification with 2,6-dichlorobenzoyl chloride[9] (1.5 equiv of pyridine, 105 °C, 2 h) gave ester **6**, *m/e* 445 (M + 1)$^+$, $[\alpha]^{22}_D$ +28.6° (*c* 2.1, benzene), after purification by silica gel chromatography (1:4 ethyl acetate–petroleum ether).

Cyclization of (*S*)-(+)-**6** was best achieved with sodium hydride (2 equiv in 2.6:1 THF–DMF, 55–60 °C, 9 h) which gave, after chromatography on silica gel (5:95 ethyl acetate–benzene), a 70–80% yield of diethyl 2-*trans*-1-propenylcyclopentane 1,1-dicarboxylate (**7**). The structure of **7**-$[\alpha]^{22}_D$ +29.6° (*c* 2.1, benzene), was supported by the ^1H and ^{13}C NMR data and, as indicated on the formula, it is particularly important for the further analysis that the double bond in **7** is clearly trans.

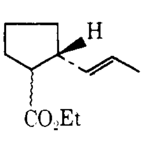


6



7 (J_{AB} = 15 Hz)

E = $CO_2C_2H_5$



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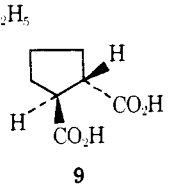

9

Absolute Configuration of 7. The appreciable rotation of the cyclization product **7** suggests strongly that the reaction must be concerted with considerable bias, whether in favor of syn or anti displacement. This was confirmed by studying the ^1H NMR spectrum of **7** in presence of the optically active shift reagent tris[(3-heptafluorobutyryl)-camphorato-*d*]europium(III).[10] The proton labeled H_A in **7** gave separate doublets (irradiation of methyl) for the two antipodes in the ratio ~72:28. Since the ratio of the two antipodes of the starting

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