methyl ether (11) (mp 116–117°; nmr (CDCl₃) δ 7.67 (d, 1, J = 2 Hz, C=CHO), 6.35 (broad s, 1, exchanges with D₂O), 5.9–5.1 (m, 4, –CH=CH_2 and HOCHO), 4.92 (d, 1,- J = 3 Hz, OCHO), 3.50 (s, 3, –OCH_3); mass spectrum m/e 226 (M⁺)). The product ratio depends on the reaction time and the amount of base used. A fourfold excess of the base and a reaction time of 20 sec led to 10 in 67% yield (only a trace of 11 was found) while a 2.5-fold excess and 120 sec gave a mixture of 10 (40%) and 11 (47%). Reduction of 11 with excess sodium borohydride at 20° in methanol afforded after distillation sweroside aglucone O-methyl ether (12): bp 105° (bath) (0.01 mm); nmr (CDCl₃) δ 7.67 (d, 1, J = 2 Hz, C=CHO), 5.1–5.8 (m, 3, –CH=CH_2), 4.91 (d, 1, J = 2 Hz, OCHO), 4.6–4.1 (m, 2, CCH_2O), 3.50 (s, 3, –OCH_3); mass spectrum m/e 210 (M⁺).

In order to investigate the fragmentation of the p-toluenesulfonate of the cis 1,3-diol, we converted 4 into the diacetate 7.[6] Hydrolysis to the diol 8 (Ba(OH)₂, anhydrous MeOH, 20°, 96%) and selective tosylation of the primary hydroxy group gave 9 (TsCl, pyridine, 8°, 92%), in which the same stereochemistry is present as in natural loganin (1). Treatment of 9 with various bases gave neither fragmentation nor elimination but by intramolecular nucleophilic substitution only an oxetane 13:[8] nmr (CDCl₃) δ 5.24 (d of d, 1, J = 5, 5 Hz, –CHO), 4.84 (d of d, 1, J = 7, 6 Hz, –CHO), 4.17 (d of d, 1, J = 6, 4 Hz, –CHO); mass spectrum m/e 240 (M⁺). The yield was over 95% using sodium methylsulfinylmethide in dimethyl sulfoxide or potassium $tert$-butoxide in $tert$-butyl alcohol as base at 20° for 120 sec.

These results show that the postulated biogenetic pathway of secologanin (3) via hydroxyloganin (2) with cis orientated substituents at C-6 and C-7 is at least not realizable in $vitro$. The biogenetic significance of 6-epi-hydroxyloganin with trans orientated substituents at C-6 and C-7 in 2 is currently under investigation.

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(8) In some cases oxetanes can be cleaved regiospecifically to alkenes and aldehydes, see G. Jones II, S. B. Schwartz, and M. T. Marton, *J. Chem. Soc., Chem. Commun.*, 374 (1973).

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Preparation and Reactions of a Titanium(IV) Metallocycle. Formation of Cyclopentanone from Ethylene and Carbon Monoxide[1]

Sir:

The chemistry of transition metal alkyls is dominated by the (frequently reversible) β elimination of metal hydrides. We recently established that the rate of

platinum(II) hydride elimination from tetra- and pentamethylenebis($tert$-phosphine)platinum(II) complexes is strongly inhibited relative to that of acyclic analogs, presumably as a result of the inability of the metallocyclic complexes to achieve the 0° M–C–C–H dihedral angle most favorable for metal hydride elimination.[2] If an unusually slow rate of metal hydride elimination were to prove a general characteristic of metallocycles, these compounds might display unusual types of reactions, normally masked by the hydride elimination in analogous acyclic organometallics. Here we wish to report the synthesis of a new metallocycle, dicyclopentadienyltetramethylenetitanium(IV) (1), and to describe several reactions of this substance that do not have close analogy in the chemistry of similar acyclic titanium(IV) alkyls.

Reaction of Cp₂TiCl₂ with 1,4-dilithiobutane in diethyl ether at –78° yields 1.[3] This compound is stable only below –30°; its purification was accomplished by removal of ether from the reaction mixture under vacuum, extraction of the residue with pentane, and chromatography of the pentane extract on Woelm Activity I alumina. All operations were performed below –40° under nitrogen or argon. Compound 1 was obtained as a bright orange solid; its yield was ∼20% based on Cp₂TiCl₂, as determined by proteolysis to butane or bromination to 1,4-dibromobutane ($vide$ $infra$). It can be recrystallized with difficulty from pentane at –100°; the properties of 1 before and after recrystallization are indistinguishable.

Elemental analysis of 1 is precluded by its thermal instability. Its solubility is sufficient to show a resonance due to the Cp protons as a sharp singlet in the nmr spectrum at δ 6.20 (CF₂ClCCl₂F); the methylene region of the spectrum is obscured by residual ether and pentane from its preparation. Its structural assignment rests on the reactions outlined in Scheme I. Reactions of 1 with HCl or bromine yield the expected butane or 1,4-dibromobutane; these reactions are assumed to proceed in high yield and provide our method of assay for 1 in solutions following chromatographic purification. Carbonylation of 1 at –40° in Et₂O (CO pressure = 10 atm), followed by gradual warming of the reaction mixture to room temperature over several hours, generates cyclopentanone in 80% yield.[4] Careful reaction of a pentane solution of 1 with carbon monoxide (1 atm) at –78° for 1 hr precipitates compound 2 as a bright yellow solid in 75% yield; this substance is assigned the structure of a carbon monoxide insertion product on the basis of ir (C=O stretch at 1730 cm⁻¹) and nmr (CD₂Cl₂) δ 6.25 (s, 10 H, Cp), 1.0–2.5 (m, 8, (CH₂)₄). Compound 2 can be recrystallized from toluene at low temperature. It decomposes at room temperature on standing as a solid or in solution; its half-life in CH₂Cl₂ is ∼15 min at 35°. When 2 is heated briefly in toluene to 70°, cyclopentanone is generated as the major volatile product.

The chemistry of 1 contrasts markedly with that of an acyclic analog, Cp₂TiBu₂ (3), in several respects.

(2) J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Amer. Chem. Soc.*, **95**, 4451 (1973).
(3) Similar preparations have been employed for Cp₂Ti(CH₃)₂ [K. Claus and G. Bestian, *Ann. Chem.*, **654**, 8 (1962)] and Cp₂Ti(CH₂Ph)₂ [H. J. deLiefde Meijer and F. Jellineck, *Inorg. Chim. Acta*, 4, 651 (1970)].
(4) Cp₂Ti(CH₂Ph)₂ has been converted to dibenzyl ketone on carbonylation: G. Fachinetti and C. Floriani, *J. Chem. Soc., Chem. Commun.*, 654 (1972).

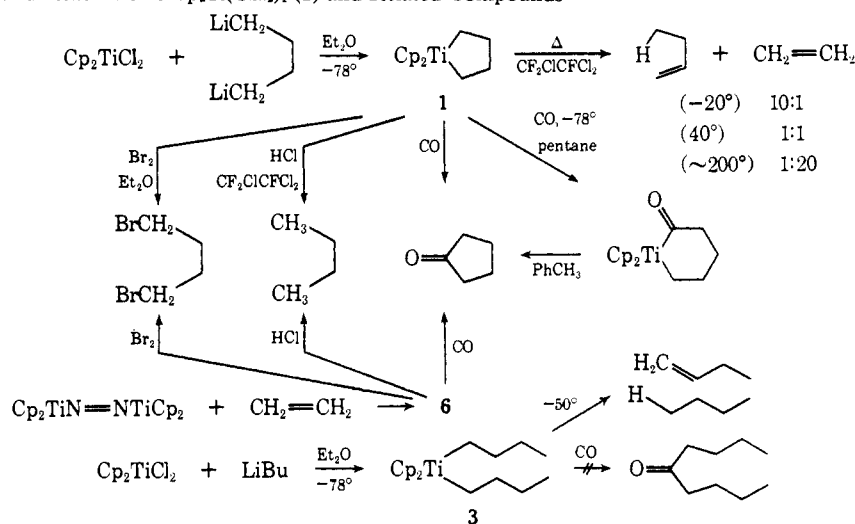Scheme I. Formation and Reactions of Cp₂Ti(CH₂)₄ (1) and Related Compounds

First, metallocycle **1** is much more stable than **3**; **1** decomposes slowly at −30° and has a half-life of several minutes at +25°; **3** decomposes rapidly at −50°. Second, certain of the products of thermal decomposition of **1** must be produced by a different mechanism than those of **3**. Compound **3** yields butane and 1-butene on decomposition, presumably by a mechanism broadly analogous to that established for di-*n*-butyl-bis(triphenylphosphine)platinum(II).[5] In contrast, **1** yields both the analogous 1-butene and ethylene. Although the mechanism of formation of the latter compound has not been established, it probably involves a carbon–carbon bond cleavage encouraged by the ∼0° Ti–C–C–C dihedral angle.[6,7] Finally, **3** decom-

poses rather than carbonylating under conditions that transform **1** to cyclopentanone.

The observation that ethylene is formed by carbon–carbon bond cleavage on thermal decomposition of **1** prompted us to try to detect the reverse reaction (**5** → **1**); related reactions have been observed previously with strained olefins.[8] Reaction of Cp₂TiN₂TiCp₂[9] with excess ethylene in toluene or ether below −30° afforded reaction mixtures whose properties strongly suggest the presence of titanium metallocycles (Scheme I). Thus, reaction of the crude mixtures with bromine, HCl, or carbon monoxide yielded products containing the tetramethylene moiety in yields up to 15%, based on Cp₂TiN₂TiCp₂. The structure of the precursor of these products, designated **6** in Scheme I, has not been determined, and efforts to isolate **6** have so far been

(5) G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 5258 (1972).

(6) The crystal structure of L₂Pt(CH₂)₄ has been reported by C. G. Biefield, H. A. Eick, and R. H. Grubbs, *Inorg. Chem.*, **12**, 2166 (1973).

(7) Related fragmentation reactions have been invoked in transition metal catalyzed rearrangements of strained rings [L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970)] and in olefin metathesis [R. H. Grubbs and T. K. Brunck, *ibid.*, **94**, 2538 (1972)].

(8) A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *J. Amer. Chem. Soc.*, **95**, 597 (1973); R. Noyori, T. Ishigami, N. Hayashi, and H. Takaya, *ibid.*, **95**, 1675 (1973).

(9) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1219 (1972).

unsuccessful; nonetheless, the similarity in reactivity and properties of **6** and **1** suggests that they are identical.

The chemistry of **1** and **3** provides a concrete demonstration of the proposition that metallocycle formation may encourage unusual reactions of transition metal alkyls by suppressing metal hydride elimination. The formation of a metallocycle (**6**) from ethylene indicates that it should be possible to prepare representative metallocycles directly from olefinic precursors. Together, these observations suggest that it may prove practical to devise new synthetic reactions—using olefins as starting materials and metallocycles as intermediates—that differ in useful ways from those involving intermediate metal hydrides.

(10) John A. Lyons Fellow, 1972–1974.

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Stereochemistry of the Electrophilic Ring Opening of Cyclopropanes by D⁺. Evidence for an Unsymmetrical, Nonrotating, Corner-Protonated Cyclopropane

Sir:

Although a number of studies have been carried out on the stereochemistry of the opening of cyclopropanes by a proton, none has examined the stereochemistry alone, uncomplicated by the question of which bond in the molecule is most susceptible to attack.[1] We have recently shown, for example, that except in completely symmetrical systems the stereochemistry of electrophilic opening of cyclopropanes by mercuric acetate is controlled by the nature and stereochemistry of the ring substituents.[2] We now wish to report two stereochemical studies on cyclopropanes in which the direction of attack by the electrophile, D⁺, does not effect the results, so that the true, intrinsic reaction stereochemistry is revealed.

The first example studied was *cis*-1,2,3-trimethylcyclopropane (**1**), which was allowed to react for 1 hr

(1) For a review see C. H. DePuy, *Fortschr. Chem. Forsch.*, **40**, 74 (1973).

(2) C. H. DePuy and R. J. McGirk, *J. Amer. Chem. Soc.*, **95**, 2366 (1973).