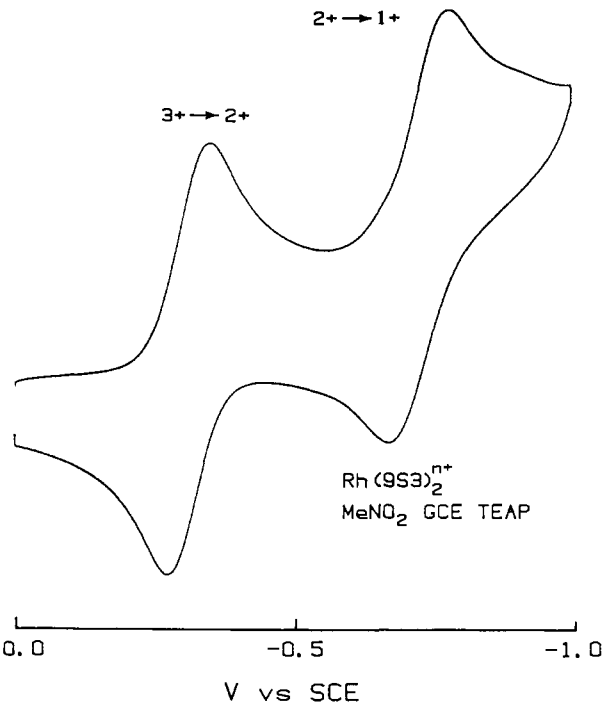

Figure 2. Cyclic voltammogram of $[Rh(9S3)_2](CF_3SO_3)_3$ in $MeNO_2$ (0.1 M Et_4NClO_4) at a glassy carbon electrode (scan rate 50 mV/s).

hyperfine splitting (line width = 40 G). Frozen solutions (77 K) yield rhombic spectra with $g_1 = 2.085$, $g_2 = 2.042$, and $g_3 = 2.009$, where g_1 reveals ^{103}Rh ($I = 1/2$, 100%) hyperfine splitting of 12×10^{-4} cm^{-1}. In a situation analogous to that recently found for the isoelectronic complex $[Co(9S3)_2]^{2+}$,[4,5] the g value pattern of $[Rh(9S3)_2]^{2+}$ (g_1, $g_2 > 2$; $g_3 \approx 2$) probably reflects a d_{z^2} ground state, consistent with axial elongation of this Jahn-Teller active d^7 ion.

The exceptional stability of $[Rh(9S3)_2]^{2+}$ with respect to disproportionation ($K_{disp} = 10^{-7}$, calculated from $E(Rh^{III}/Rh^{II}) - E(Rh^{II}/Rh^{I})$ apparently derives from both the electronic and steric properties of this crown thioether. Thioethers generally stabilize low oxidation states by virtue of their π-acidity. Thus $[Cu(SR_2)_6]^{2+}$ complexes, for example, have the highest redox potentials known for the (Cu^{II}/Cu^{I}) couple of this element.[3,13] Hence 9S3 presumably electronically destabilizes Rh(III) with respect to Rh(II) and Rh(I). On the other hand, the rigid conformation of 9S3 ensures that any bis complex of this ligand has six thioether groups in close proximity to the metal. The imposition of a six-coordinate environment would tend to destabilize Rh(I), which usually adopts square planar coordination geometry. These cross-cutting effects evidently suffice to buckle the free energy profile such that Rh(II) is no longer at a relative maximum with respect to Rh(III) and Rh(I) but rather a relative minimum. At the same time, 9S3 apparently inhibits the usually rapid dimerization of Rh(II); EPR and electrochemical studies show that $[Rh(9S3)_2]^{2+}$ decays (presumably by dimerizing) with a half-life greater than 0.5 h.

Further studies addressing the generality of this unusual stabilization as well as the reactivity of the resulting novel species will be reported shortly.

Acknowledgment. We are grateful to Richard Brownsword for experimental assistance. Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society and to the Science and Engineering Research Council (U.K.) for support of this research.

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Supplementary Material Available: Tables S1-S6 listing crystallographic details, final atomic coordinates, bond lengths and angles, hydrogen atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, and torsional angles (5 pages); tables of observed and calculated structure factors (8 pages). Ordering information is given an any current masthead page.

Photochemistry of Titanacyclobutanes. Evidence for a Metal-Centered 1,4-Biradical Intermediate

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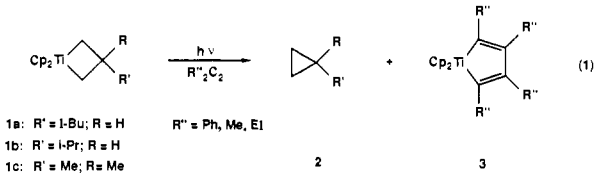
Metallacycles are key intermediates in organometallic chemistry and catalysis as well as useful reagents for organic synthesis.[1] Despite numerous studies on the preparation and thermal chemistry of these complexes, few photochemical investigations have been reported.[2,3] In this paper, we report photochemical studies of the bis(cyclopentadienyl)titanacyclobutanes **1**.[4] Photochemical activation of **1** results in clean reductive elimination to form cyclopropanes and titanocene which can be trapped by a number of added reagents. Stereochemical studies strongly suggest a stepwise mechanism in which the primary photochemical step involves metal-carbon bond homolysis to produce a metal-centered 1,4-biradical intermediate.

Photolysis of the d^0, 16-electron titanacyclobutanes[5] **1** in aromatic, hydrocarbon, or ether solvents in the presence of disubstituted acetylenes[6a] produces cyclopropane[6b] **2** and the bis(cyclopentadienyl)titanacyclopentadiene[6c] **3** (independent of irradiation wavelength over range 250-550 nm). The mass balance



between the products (cyclopropane and **3**) and starting material **1** is essentially quantitative (>95% by NMR). This photochemically induced reductive elimination[8] contrasts with the well-

(1) (a) Casey, C. P. *React. Intermed.* **1981**, *2*, 135. (b) Grubbs, R. H. *Compr. Organomet. Chem.* **1982**, *8*, 499. (c) Puddephatt, R. J. In *Inorganic Chemistry Towards the 21st Century*; Chisholm, M. H., Ed.; ACS Symposium Series 211; American Chemical Society: Washington, DC, 1983; p 353.

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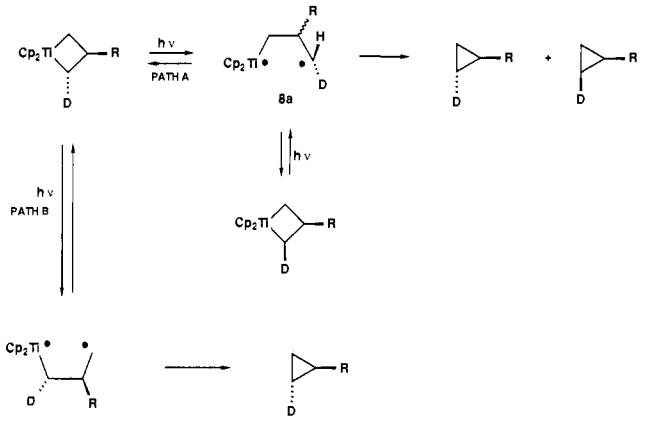
(5) UV-vis spectroscopy of **1a**: λ_{max} (pentane, THF) 490 nm ($\epsilon \sim 1500$ M^{-1} cm^{-1}), 350 nm, and 240 nm. LMCT transitions (i.e., Cp → M) by analogy to Cp_2TiX_2 complexes: Lauher, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. Bruce, M. R. M.; Kenter, A.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 639.

(6) (a) Concentrations for all photochemical experiments ranged from 50 to 140 mM in metallacycle and 75 to 600 mM in trapping agent. (b) Characterized by ^1H NMR and gas chromatography. (c) Characterized by ^1H NMR, ^{13}C NMR, and UV-vis spectroscopy: ref 10 and 16f. Also: Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1178.

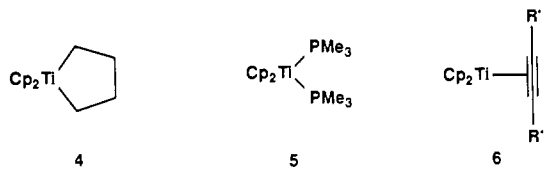
(7) Review: Pez, G. P.; Armor, J. N. *Adv. Organomet. Chem.* **1981**, *19*, 1.

0002-7863/87/1509-6182$01.50/0

Scheme I



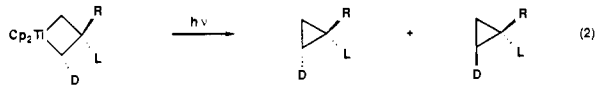
documented thermal chemistry which involves retro 2 + 2 cleavage to titanocene methylidenes and olefins (i.e., metathesis chemistry).[4] Metallacyclopentane **4** is produced when excess ethylene is used



4 5 6

as the trapping reagent.[9a] Photolysis of **1** and PMe_3 resulted in the bis(phosphine)[9b] adduct **5**. Low-temperature photolysis (<−20 °C) of **1** and disubstituted acetylenes (R′ = Ph, *t*-Bu, $SiMe_3$) lead to the formation of the monoacetylene[10] adducts **6**.

The mechanism of the photoinduced reductive elimination was investigated by stereochemical studies. Photolysis (at −20 °C) of the stereospecifically deuteriated titanacyclobutanes **7a**, **7b**, and **7c** employing Ph_2C_2, PMe_3, or no trapping agent in either toluene



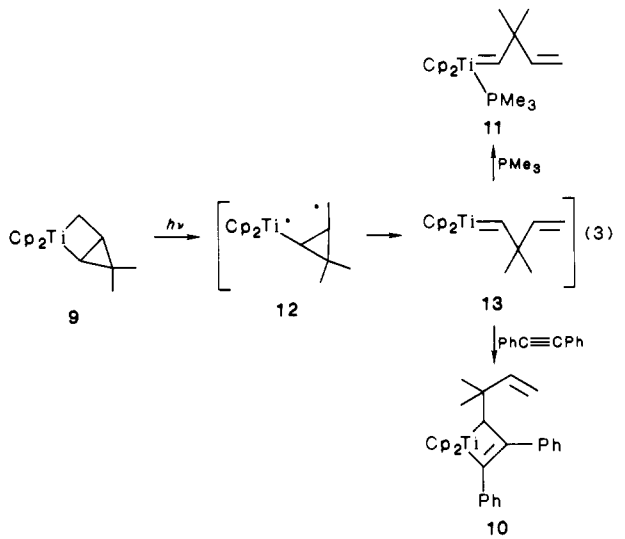
(2)

7a: R = *t*-Bu; L = H 8a-E 8a-Z
7b: R = *i*-Pr; L = H 8b-E 8b-Z
7c: R = *i*-Pr; L = D 8c-E 8c-Z

or tetrahydrofuran yields both cyclopropane stereoisomers **8-*E*** and **8-*Z***, with the predominant isomer resulting from retention of stereochemistry (i.e., **8-*E***). The stereochemistry of the reactant titanacyclobutanes[4] and the product cyclopropanes[11] was monitored by ^1H and ^2H NMR spectroscopy throughout the photolysis. The product ratio **8-*E*/8-*Z*** decreased monotonically from an initial value of greater than 5:1 to a final ratio of ca. 3:1 during photolysis. Moreover, the metallacyclobutane starting material was found to isomerize during the course of the photochemical reaction tending toward complete isomerization at high conversion. These results, particularly the loss of stereochemical integrity of the reactant, are inconsistent with a concerted reductive elimination and strongly suggest a stepwise mechanism involving initial homolytic cleavage to a 1,4-biradical intermediate. This intermediate can recombine after rotation to generate isomerized starting material or cleave to produce cyclopropane and Cp_2Ti (Scheme I). The product distribution and the rate of isomerization of the reactant metallacyclobutane were identical in toluene-d_8 and THF-d_8 arguing against the intervention of zwitterionic intermediates.[12] Moreover, the results were found to be indepdendent of the nature and concentration of the trapping agent indicating that these reagents serve only to capture the presumed organometallic photoproduct titanocene and are not involved in organic product-determining steps.

If the stepwise mechanism is responsible for all of the product formed, then the observed product ratio of greater than 3:1 (**8-*E*/8-*Z***) leads us to conclude that carbon–carbon bond formation from the 1,4-biradical to yield cyclopropane proceeds with retention (path B). Although S_H2 reactions generally proceed with inversion,[13] it is possible that the Ti d orbitals play an important role in controlling the stereochemistry of the ring closure from the metal-centered biradical. If rotation of the biradical were much faster than cyclopropane extrusion (path A) *and* the rates of cleavage via paths A and B were identical (i.e., no secondary isotope effect for homolysis), then the initial product ratio **8-*E*/8-*Z*** would be 3:1. The observed initial ratio of >5:1 implies (a) a secondary isotope effect in the homolysis of the metal–carbon bond which, as expected,[14] favors cleavage of the nondeuteriated C–Ti bond (i.e., retention via path B) *and* (b) that extrusion of cyclopropane from the 1,4-biradical is competitive with rotation.[13] Another explanation which cannot be definitively ruled out at present is that the product cyclopropane stereochemistry results from competition between a stepwise pathway and a concerted elimination that proceeds with retention.

Further evidence for the biradical mechanism was found in the photolysis of the bicyclic[15] metallacycle **9** which, in contrast to **1**, photochemically cleaves in a formal 2 + 2 fashion to yield the metallacyclobutene **10** and the alkylidene phosphine adduct **11** in the presence of diphenylacetylene and PMe_3, respectively. The most plausible explanation for this difference in reactivity is that the 1,4-biradical intermediate **12** cleaves via a cyclopropylcarbinyl radical rearrangement to the putative alkylidene **13** which is trapped to give the observed photoproducts.



(3)

9 12 13 11 10

The stepwise pathway also provides a unifying mechanism for the photochemistry of both the titanacyclobutanes and the extensively studied group 4 dialkyl complexes which do not reductively eliminate. Our work further substantiates that the primary photoprocess involves metal–carbon bond homolysis. For acyclic systems, a number of products are observed depending on reaction conditions; this behavior probably arises from competing reactions of an intermediate radical cage complex.[2,16] For the

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(11) Assignments by difference NOE techniques. Also: Schaeffer, T.; Sebastian, R.; Wasylishen, R. E. *Can. J. Chem.* **1982**, *60*, 845.
(12) Preliminary work reveals that the product cyclopropane stereochemistry in acetonitrile is within experimental error of the results for toluene and THF.
(13) For example: (a) Johnson, M. D. *Acc. Chem. Res.* **1983**, *16*, 343. (b) Dodd, D.; Johnson, M. D.; Lockman, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 3663. (c) Incremona, J. H.; Upton, C. J. *J. Am. Chem. Soc.* **1972**, *94*, 301.
(14) Melander, L.; Saunders, W. H. *Reactions of Isotopic Molecules*; Wiley: New York, 1980.
(15) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721.

titanacyclobutanes, extrusion of cyclopropane provides a very fast intramolecular trap for the analogous 1,4-biradical intermediate.

Current efforts are directed at characterizing monomeric titanocene by low-temperature spectroscopy, developing the reaction chemistry of this and other photochemically generated intermediates, and further probing the mechanistic details. We are also investigating the photochemical reactivity of other group 4 metallacycles.

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Stereochemical Fate of *O*-Methyl Groups in the Biosynthesis of Protoberberine Alkaloids

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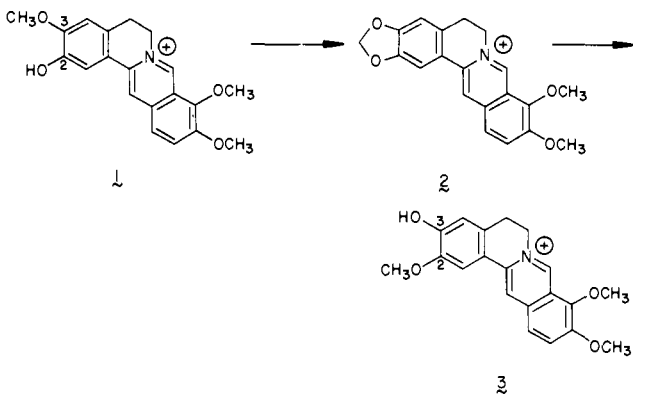
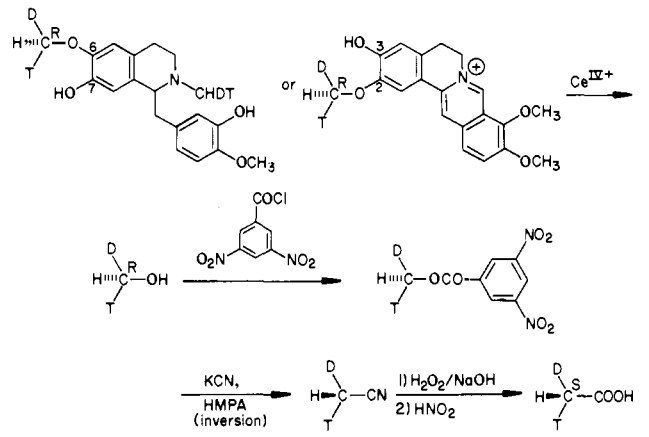
The formation of the medicinally important benzylisoquinoline alkaloid berberine (**2**) from one molecule each of dopamine and *p*-hydroxyphenylacetaldehyde, both in turn derived from tyrosine,[1] involves eight enzymes which have recently been purified and characterized.[2] The terminal step in this sequence is the formation of **2** from columbamine (**1**). This reaction, catalyzed by the Fe^{2+}-dependent enzyme berberine synthase,[3] is one of a number of examples of the formation of a methylenedioxy bridge by oxidative cyclization of an *o*-methoxy phenol precursor[1,4,5] either by an ionic or a radical mechanism.[1,4,6] An intriguing further transformation of **2** leads to jatrorrhizine (**3**),[7,8] the major alkaloid of *Berberis* cell cultures. This conversion was shown[8] to involve a ring opening of the methylenedioxy bridge to give the 2-methoxy group of **3** (Scheme I). To obtain more information on the

Scheme I



Scheme II



mechanisms of these transformations, we traced the stereochemical fate of the chiral methyl group of *S*-adenosylmethionine (AdoMet) through the reaction sequence leading to **3**.

Samples of (*methyl-R*)- and (*methyl-S*)-[*methyl*-^{2}H,^{3}H]-AdoMet[9,10] (100 and 160 mCi/mmol, 91% and 86% ee) were used as substrates in the *O*- and *N*-methylation of 4′-*O*-methylnorlaudanosoline catalyzed by the 6-*O*-[11] and *N*-methyltransferases[12] isolated from *Berberis*[12] cell cultures, respectively. The resulting samples of (1*S*)-[6-*O*,*N*-methyl-^{2}H,^{3}H]reticuline were degraded as shown in Scheme II[10] to convert the 6-*O*-methyl group stereospecifically into the methyl group of acetic acid for chirality analysis by the method of Cornforth[13] and Arigoni.[14] The *F* values[15] of the resulting acetic acid samples were 75.6 and 25.1, respectively. Since the degradation sequence involves one inversion of configuration, these values indicate 88% ee *S* configuration and 86% ee *R* configuration, respectively, for the 6-*O*-methyl group of the two reticuline samples. Hence, the transfer of the methyl group of AdoMet has occurred cleanly with inversion of configuration. This stereochemistry conforms to that established for most methyltransferases studied to date.[16,18,19]

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‡ Universität München.

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(18) Floss, H. G. In *Mechanisms of Enzymatic Reactions: Stereochemistry*; Frey, P. A., Ed.; Elsevier: Amsterdam, 1986; pp 71-88.

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