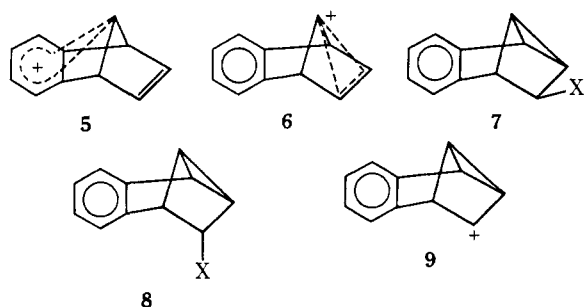


di- π -methane rearrangements) to derivatives of 4-benzotricyclo[4.1.0.0^{3,7}]heptene, 7-H (or 8-H). Furthermore, Tufariello and Rowe⁸ showed that photorearrangements of 1-X isomers give exo 2-tricyclic compounds 7-X, while those of 2-X give endo 2-epimers 8-X. It was known^{3,9} that 8-X species rearrange thermally to 2-X isomers, but, more pertinent to this work, Tufariello and Rowe showed that exo isomers 7 also rearrange to the syn (2-X) derivatives, when cationic processes are involved. Thus 9 (or a variant thereof) which presumably is formed from 7-X leads, before capture of the cation, to 6, which gives^{3,4} *syn*-2-X products (either of rearrangement or solvolysis).



Such a mechanism could be demonstrated (or rejected) by carrying out the irradiation under conditions where 7 isomers are stable. Indeed 1-Cl, when irradiated at 35° directly¹⁰ in hexane, or with photosensitization in acetone, gave a mixture of 2-Cl and 7-Cl. That the primary photoproduct was 7-Cl was established by following the disappearance of 1-Cl and the production of 2-Cl and 7-Cl. During irradiation, 7-Cl appeared immediately (pmr analysis¹¹⁻¹³), followed by slower appearance of 2-Cl. The 7-Cl to 2-Cl transformation was a thermal reaction, occurring equally well in the dark or light, while the disappearance of 1-Cl and formation of 7-Cl required photoexcitation.¹⁴

When 1-Br was irradiated at room temperature, only 2-Br was noted. However, irradiation in acetone-*d*₆ at -70° led to a mixture comprising mainly 7-Br with some 2-Br, which upon warming isomerized completely to 2-Br. Addition of methanol at -70° to a partially photoisomerized sample of 1-Br in *n*-pentane gave 2-

(8) J. J. Tufariello and D. W. Rowe, *J. Org. Chem.*, **36**, 2057 (1971).

(9) G. W. Nachtigall, Ph.D. Thesis, University of Colorado, 1968.

(10) Edman⁷ gave convincing evidence that his photorearrangements involved triplets, and we assume that this is true for our compounds, even under direct irradiation. The heavy atom (chlorine or bromine) may promote rapid intersystem crossing.

(11) The pmr spectrum of 7-Cl, isolated pure by irradiation of 1-Cl at 5° in 3:1 benzene-acetone, lacked olefinic absorptions and had two aromatic peaks (ratio 3:1), indicating an unsymmetrical tetracyclic skeleton. Comparison of this spectrum to those of other 7 and 8 derivatives confirmed the structure assignment. The exo stereochemistry of the chlorine atom at C-2 was assigned by noting that the exo C-2 proton in compounds of the general structure 8 appear in pmr spectra as four-line patterns,^{2,8,12} whereas the endo C-2 protons in compounds 7 appear as doublets^{7,8,13} (7-Cl, CCl₄, δ 3.41, d, $J = 3.5$ Hz).

(12) S. J. Cristol and J. I. Maxwell, *J. Org. Chem.*, **39**, 228 (1974).

(13) J. I. Maxwell, unpublished results.

(14) While 2-Cl appeared to be photoinert upon direct irradiation in hexane, or upon photosensitization in acetone or in acetone-benzene mixtures, its photoisomerization would give 8-Cl, which can be anticipated^{2,15,16} to be unstable at room temperature and to rearrange rapidly to 2-Cl. The photomethanolysis of 2-Br is consistent with this.

(15) J. J. Tufariello and R. J. Lorence, *J. Amer. Chem. Soc.*, **91**, 1546 (1969); J. J. Tufariello and D. W. Rowe, *J. Chem. Soc., Chem. Commun.*, 1066 (1972).

(16) J. Lhomme, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 1548 (1969).

OCH₃ from 7-Br but did not affect the unrearranged 1-Br.

In addition, photoisomerization of 1-Cl at 5° in acetone-benzene, followed by treatment with 4 *M* sodium methoxide in methanol, gave an 83:17 mixture of 8-OCH₃ and 2-OCH₃. As this mixture was identical with that^{3,9} produced by the ground-state solvolysis of 2-Cl in a comparable medium, the intermediacy of the cation 6 in the thermal portion of these "photosolvolyses" is confirmed.

Irradiation of either 7-bromonaphthonorbornadiene in inert solvents led to pure *syn* bromide 4-Br, and irradiation of 3-Br in methanol gave pure *syn* ether 4-OCH₃. Thus these followed the same pattern as the benzonorbornadienes.

Our experiments lead us to conclude that it is likely that the "photosolvolyses," the photoepimerization, and the "photostability" of 2 and 4 in inert solvents are all manifestations of one primary photoprocess, a di- π -methane rearrangement. Subsequent ion pair formation precedes either internal return to 2-X or 4-X or solvolysis to 2-OCH₃ or 4-OCH₃. While we have not demonstrated that the "photostability" of the *syn* isomers is due to the reversible 2 \rightleftharpoons 8 transformation or that other diradical or homoallyl to cyclopropylcarbinyl transformations do not occur in the 1 to 7 isomerization, the ubiquitousness of the di- π -methane rearrangement¹⁷ make alternative formulations highly speculative. Appropriate labeling experiments can distinguish such alternatives, as the di- π -methane rearrangement leads to carbon-scrambling of a predictable nature.^{7,8,17,18}

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The Structure of "Titanocene." Clarification by Carbon-13 Nuclear Magnetic Resonance

Sir:

It has been known for some time that reduction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ or $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$ yields a green dimeric compound conforming to the stoichiometry required for "titanocene." The structure of this green dimeric form of "titanocene" has been the subject of

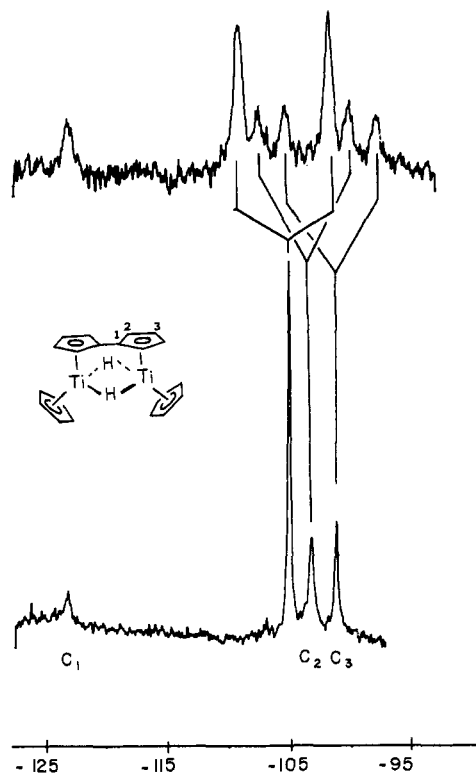
(1) G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *J. Amer. Chem. Soc.*, **88**, 1138 (1966), and references therein.

(2) K. Clauss and H. Bestian, *Justus Liebig's Ann. Chem.*, **654**, 8 (1962).

Table I. ^{13}C Nmr Chemical Shifts^a for "Titanocene" and Model Compounds^b

Compounds	δC_1	δC_2^b	δC_3^b	$\delta(\eta^5\text{-C}_5\text{H}_5)$	$\delta(\text{C}_2\text{-C}_3)$
$(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Mo-}\mu\text{-}$ $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4)\text{-Mn}(\text{CO})_4^c$	<i>d</i>	-104.5	-86.0	-82.9	18.5
$(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{W-}\mu\text{-}$ $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4)\text{-Mn}(\text{CO})_4^c$	<i>d</i>	-100.8	-81.3	-78.7	19.5
$[(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)_2\text{Co}_2(\text{III,III})\text{-}$ $[\text{PF}_6]_2]^f$	-111.2	-85.7	-83.0		2.7
"Titanocene" ^g	-122.6	-102.7	-100.4	-104.6	2.6

^a The spectra were obtained at 22.631 MHz on a Bruker HFX-90 interfaced with a Digilab FTS/NMR-3 data system. Chemical shifts are in ppm relative to external TMS and are believed to be accurate to ± 0.1 ppm. A positive chemical shift represents a nucleus more shielded than that in the reference. ^b Assignments to C_2 and C_3 are ambiguous and may be reversed. ^c In CH_2Cl_2 solution. ^d These resonances were not observed, even after addition of $\text{Cr}(\text{acac})_3$. ^e In benzene solution. ^f In DMSO solution: A. Davison and J. C. Smart, *J. Organometal. Chem.*, **49**, C43 (1973). ^g In THF solution. ^h These model compounds were chosen because their ^1H nmr spectra show that there is magnetic equivalence for the pair H_2 , H_5 , and H_3 , H_4 . In both of the proposals for "titanocene" a mirror plane is present. This requirement excludes niobocene,^{6b} tantalocene,^{6b} and $[(\text{C}_5\text{H}_5)\text{Ti}]_2(\text{H})(\text{H}_2\text{AlEt}_2)(\text{C}_{10}\text{H}_8)$.⁷

**Figure 1.** The ^{13}C and $^{13}\text{C}\{-^1\text{H}\}$ nmr spectra of "titanocene."

considerable debate.³ We wish to report unambiguous spectroscopic proof that "titanocene" is $\mu\text{-}(\eta^5\text{-}\eta^5\text{-fulvalene})\text{-di-}\mu\text{-hydrido-bis}(\text{cyclopentadienyltitanium})$.

Brintzinger and Bercaw⁴ have shown on the basis of chemical and infrared evidence that "titanocene" deviates from a normal metallocene structure in that the dimer contained two bridging hydrides and two C_5H_4 ligands bound in an unknown manner. Subsequently, it was suggested that the C_5H_4 ligands may be complexed as $\mu\text{-}(\eta^5\text{-}\eta^1\text{-cyclopentadienyl})$ units as in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Mo-}\mu\text{-}(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4)\text{-Mn}(\text{CO})_4$ ⁵ and niobocene.⁶ However, Guggenberger and Tebbe⁷ have pre-

sented strong chemical evidence that the C_5H_4 units were present as a $\mu\text{-}(\eta^5\text{-}\eta^5\text{-fulvalene})$ ligand, like those in $[(\text{C}_5\text{H}_5)\text{Ti}]_2(\text{H})(\text{H}_2\text{AlEt}_2)(\text{C}_{10}\text{H}_8)$ and $[(\text{C}_5\text{H}_4)\text{Ti-HAlEt}_2]_2(\text{C}_{10}\text{H}_8)$, whose structures were determined by X-ray studies. Since model compounds containing the

 $\mu\text{-}(\eta^5\text{-}\eta^1\text{-cyclopentadienyl})$ $\mu\text{-}(\eta^5\text{-}\eta^5\text{-fulvalene})$

features shown above were available, we undertook a ^{13}C nmr investigation to determine whether a $\mu\text{-}(\eta^5\text{-}\eta^5\text{-fulvalene})$ ligand was distinguishable from a $\mu\text{-}(\eta^5\text{-}\eta^1\text{-cyclopentadienyl})$ ligand and if the ^{13}C nmr spectrum of "titanocene" would classify it as one or the other.

From the results in Table I it is apparent that in compounds containing a $\mu\text{-}(\eta^5\text{-}\eta^1\text{-cyclopentadienyl})$ group C_2 is shifted from C_3 by *ca.* 20 ppm, whereas in the example containing a $\mu\text{-}(\eta^5\text{-}\eta^5\text{-fulvalene})$ ligand, C_2 is shifted from C_3 by *ca.* 2 ppm. That is, metalation of the cyclopentadienyl ring increases $\delta(\text{C}_2\text{-C}_3)$ tenfold *vs.* carbon substitution. Inasmuch as σ bond transition metals frequently have a pronounced effect on proton resonances,⁸ this result was anticipated.

The ^{13}C nmr spectrum of "titanocene" in Figure 1 clearly shows the pattern characteristic of a $\mu\text{-}(\eta^5\text{-}\eta^5\text{-fulvalene})$ ligand; *i.e.*, C_2 is shifted from C_3 by *ca.* 2 ppm. Further, C_1 is shifted by ~ 25 ppm, as in bis- $(\eta^5\text{-}\eta^5\text{-fulvalene})\text{dicobalt(III,III)}$ hexafluorophosphate. Indeed, except for an overall difference in chemical shift, the spectrum is essentially superimposable with that of the cobalt complex. The structure of "titanocene," therefore, is as indicated in Figure 1. This result is in accord with the suggestions by Guggenberger and Tebbe⁷ and is one of the early proposals by Brintzinger and Bercaw.⁴

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