

are accommodated most reasonably by a charge distribution in solvolytic transition states leading to symmetrical allylic cations that reflects little 1,3 π interaction, as in **1a** or **5a**.

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(11) E. S. Lewis, R. R. Johnson, and G. M. Coppinger (*J. Amer. Chem. Soc.*, **81**, 3140 (1959)) report $(k_H/k_D)_{av} = 0.988$ for solvolysis of **4** in aqueous acetone.

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Extended Hückel Calculations Related to the Chemistry of Titanocene

Sir:

Bis(π -cyclopentadienyl) complexes of nickel, cobalt, iron, chromium, and vanadium are fairly stable compounds and easily prepared by standard methods of organometallic synthesis. Contrastingly, all attempts to synthesize the corresponding titanium compound (π -C₅H₅)₂Ti^{II} have failed thus far. There is a compound of composition C₁₀H₁₀Ti, sometimes referred to in the literature as "titanocene" (see, e.g., ref 1, 2, and earlier references quoted there). This compound, however, is in fact a dimer;¹ in addition it exhibits ir and nmr spectra which are typical of σ - rather than of π -bound C₅H₅ ligands.² Whatever the structure of this compound, it is certainly not analogous to its neighbors in the 3d series. On the other hand, certain derivatives of (π -C₅H₅)Ti^{II} do exist: (π -C₅H₅)₂Ti(CO)₂ and (π -C₅H₅)₂Ti·bipyridine appear to be normal monomeric sandwich compounds with π -bound rings.³⁻⁵ Their parent compound (π -C₅H₅)₂Ti, while apparently not persisting as a stable compound, might occur, however, as a reactive intermediate in such reactions as catalytic alkyne hydrogenations⁶ or the reduction of gaseous nitrogen.⁷ In view of its elusive nature, it appears worthwhile to investigate the behavior of the hypothetical molecule (π -C₅H₅)₂Ti at least theoretically, in the hope of obtaining some guidance for further experimental investigations on the chemical properties of this species.

One aspect in which (π -C₅H₅)₂Ti would intrinsically differ from its neighbors in the 3d series can be derived from simple symmetry rules which have recently received attention in the literature: a molecule is a potential candidate for a spontaneous distortion whenever the symmetry coordinate of that distortion connects occupied and empty molecular orbitals of not too different energies (pseudo-Jahn-Teller effect).^{8,9} From recently

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

(2) J. J. Salzmänn and P. Mosimann, *Helv. Chim. Acta*, **50**, 1831 (1967).

(3) J. G. Murray, *J. Amer. Chem. Soc.*, **83**, 1287 (1961).

(4) F. Calderazzo, J. J. Salzmänn, and P. Mosimann, *Inorg. Chim. Acta*, **1**, 65 (1967).

(5) E. O. Fischer and R. Amtmann, *J. Organometal. Chem.*, **9**, P 15 (1967).

(6) K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Jap.* **39**, 1178 (1966).

(7) E. E. Van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Åkermark, *J. Amer. Chem. Soc.* **91**, 1551 (1969).

published MO calculations on metallocenes^{10,11} it is evident that (π -C₅H₅)₂Ti is unique among the 3d transition metal sandwiches in that the a_{1g} orbital (an essentially nonbonding metal d_{z²} orbital) remains unoccupied only in the titanium derivative.¹² Closely below the a_{1g} orbital there occur ligand π orbitals of e_{1g} and e_{1u} symmetry. We can therefore suspect that titanocene is set apart from other metallocenes by an increased tendency to undergo distortions of e_{1g} and e_{1u} symmetry. Of particular interest is the possibility of a spontaneous e_{1u} distortion, which involves a bending of the two metal-ring bonds away from axial symmetry. While such an analysis is feasible by second-order perturbation theory (see, e.g., ref 13), we shall apply here the simpler method of extended Hückel calculations as a function of the molecular geometry.

The evaluation of one-electron energies and wave functions follows closely the conventional Wolfsberg-Helmholz approach, with off-diagonal terms given as $H_{ij} = k \cdot S_{ij}(H_{ii} + H_{jj})/2$ ($k = 1.75$). The program used is described elsewhere.¹⁴ In order to keep computation times within justifiable limits, the following simplifications were used (single-parameter, Slater-type atomic orbitals were used throughout). Exponents of 1.35 (Ti-4s), 1.70 (Ti-3d), 0.75 (Ti-4p), 1.65 (C-2s), 1.44 (C-2p), and 1.20 (H-1s) were taken from ref 11 and 15. Diagonal elements H_{ii} are obtained as a function of atomic charges, from the tabulations given in ref 16 (metal) and 10 (carbon, hydrogen). Self-consistency is achieved, in the case of the linear geometry, with a charge of +0.69 on the metal atom, and -0.02 and -0.05 on C and H, respectively. In the bent conformations, the metal becomes less positive, mainly due to increased occupation of the d_{z²} orbital. Instead of recycling the calculations, however, we have kept the input parameters H_{ii} constant for all geometries. We estimate that a decrease of the metal charge by 0.04-0.08 unit would produce self-consistency for the bent conformations.¹⁷ The assumed geometry is essentially the same as in previous calculations on vanadocene, except that two sets of calculations were carried out, using metal-carbon distances of 2.26 and 2.47 Å, respectively.¹² Apart from reduced repulsions between the two rings at the larger distance of 2.47 Å, both Ti-C values yield almost identical potential surfaces. Single-electron energies thus obtained for a linear (π -C₅H₅)₂Ti molecule are in agreement with recently published results of extended Hückel calculations on vanadocene.^{10,11}

(8) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968).

(9) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

(10) J. H. Schachtschneider, R. Prins, and P. Ros, *Inorg. Chim. Acta*, **1**, 462 (1967).

(11) M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **91** 3432 (1969).

(12) Although our calculations are actually based on an eclipsed sandwich structure (symmetry D_{5h}), we have labeled the molecular orbitals for the linear conformation according to symmetry D_{5d} to facilitate comparison with previous calculations reported in the literature.

(13) B. J. Nicholson and H. C. Longuet-Higgins, *Mol. Phys.*, **9**, 461 (1965).

(14) L. S. Bartell and L. S. Su, in preparation.

(15) J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *J. Chem. Phys.*, **38**, 796 (1963).

(16) H. Basch, A. Viste, and H. B. Gray, *ibid.*, **44**, 10 (1966); *Theoret. Chim. Acta*, **3**, 458 (1965).

(17) For the metal 4p_z orbital, a negative electron occupation appears in the population analysis. This is an artifact produced by the rules of the Mulliken population analysis: R. F. Fenske, K. G. Caulton, D. D. Radtke, and C. C. Sweeney, *Inorg. Chem.* **5**, 951 (1966).

Figure 1 shows the dependence of the total energy, relative to that of the linear molecule, on the angle ω between the planes of the two rings. For the 55-electron system $(\pi\text{-C}_5\text{H}_5)_2\text{V}$ a normal, almost parabolic potential well with a minimum at $\omega = 0$ is obtained. In

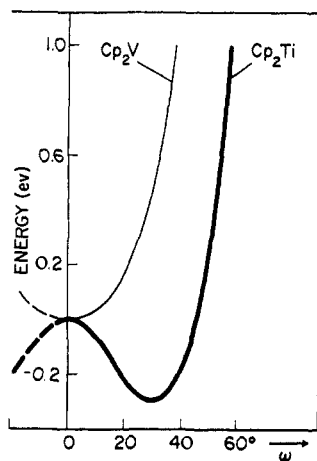


Figure 1. Total energy as a function of angle ω between the planes of the two aromatic ring ligands for $(\pi\text{-C}_5\text{H}_5)_2\text{V}$ and $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$.

contrast to this, the 54-electron species $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ exhibits a potential curve with a minimum at 30–40°. The rising part of the $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ potential function which eventually overcomes the distorting tendencies appears to originate from the steric repulsion between the two ring ligands. The essentially nonbonding molecular orbitals in the equator plane of the molecule, which accommodate the unpaired electrons in the bent $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ species, exhibit a noticeable p character, resulting in an unsymmetrical shape of these orbitals (Figure 2). The results of our calculations, crude as they are, would indicate that the interaction between filled e_{1u} ligand orbitals and an empty a_{1g} metal orbital is in fact of an order of magnitude sufficient to cause a distortion of the sandwich structure and might offer, therefore, an explanation of why the chemistry of titanocene deviates so strikingly from that of other metallocenes.

In addition to the e_{1u} distortion discussed so far, a distortion of symmetry e_{1g} will also be facilitated by an interaction of ligand π electrons with the empty a_{1g} orbital as mentioned above.¹² This kind of distortion ultimately converts the sandwich compound to a di- $(\sigma\text{-cyclopentadienyl})$ derivative. While we have not performed any calculations on the potential surface along this reaction coordinate, there can be little doubt that a $\pi \rightarrow \sigma$ conversion will be substantially easier in titanocene than in vanadocene or ferrocene.

The question we are left with at this point is then: why is the titanocene molecule not capable of extended existence, if not as an axially symmetric, then as a distorted molecule?¹³ An interesting suggestion to this point has been made by Volpin, *et al.*¹⁹ These authors

(18) It may be noted that the di- $(\pi\text{-C}_5\text{H}_5)^-$ derivatives of tin(II) and lead(II) do indeed exist as e_{1u} distorted, yet stable, monomeric sandwich species (see, e.g., L. D. Dave, D. F. Evans, and G. Wilkinson, *J. Chem. Soc.*, 3684 (1959), and earlier references quoted there).

(19) M. E. Volpin, V. A. Dubovitskii, O. V. Nogina, and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, 151, 1100 (1963).

suggest that titanocene might have a reactivity akin to that of a carbene. This view, based on the observation that $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ *in statu nascendi* reacts with 2 moles of diphenylacetylene to give a metallocyclic ditolane de-

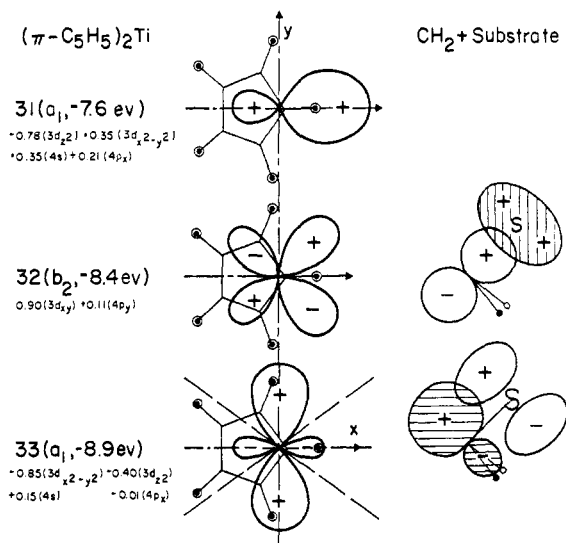


Figure 2. Schematic representation of the essentially nonbonding molecular orbitals in a bent $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ molecule ($\omega = 30^\circ$). For comparison, the corresponding orbitals of a carbene and their interactions with bonding and antibonding orbitals of a substrate are traced at the right (hatched orbitals are doubly occupied).

rivative, is couched in terms of a bonding scheme which is not in accord with present views. The results of our calculations, however, substantiate this intuitive idea.

Some of the most striking modes of reaction of a carbene are its facile insertion into σ bonds, addition to π bonds,²⁰ and its complex formation with π acceptors like CO or N_2 .^{21,22} In all these examples the smoothness of the reaction results from the possibility of simultaneous σ - and π -type interactions in the transition state. An approaching R_2C species can set up a σ interaction of its empty p orbital with a bonding orbital of the substrate, while at the same time its filled σ orbital overlaps with the corresponding antibonding orbital of the substrate.²³

From the shape of the MO's in $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ given in Figure 2, it is obvious that very similar interactions can be pictured for the species $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ in its bent conformation, with orbitals 33 (a_1) and 32 (b_2) assuming the roles of the σ and p orbitals of R_2C , respectively.²⁴ An important feature is that the two orbitals not only have an appropriate symmetry, but also a spatial extension favorable for extensive σ and π overlap. Insertion and complex formation reactions analogous to those of a

(20) See, e.g., W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

(21) Y. G. Borod'ko, A. E. Shilov, and A. A. Shteinman, *Dokl. Akad. Nauk SSSR*, 168, 581 (1966).

(22) G. von Buenau, P. Potzinger, and G. O. Schenck, *Tetrahedron*, 21, 1293 (1965).

(23) R. Hoffmann (*J. Amer. Chem. Soc.*, 90, 1475 (1968)) has pointed out that the optimal reaction path has to involve a "sidewise" attack of the R_2C species since then all the bonding MO's of the reactants correlate to bonding MO's of the products.

(24) In contrast to a carbene, however, $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ has the option of binding two ligand molecules as in $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$; this is related to the presence of a third low-lying orbital (31(a_1)) in Figure 2).

carbene might thus provide a kinetically feasible way out of the thermodynamically quite unfavorable situation of titanium(II) in $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$.²⁵ We are pres-

(25) This analogy would require that $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ be available in a singlet state. Such a low-lying singlet state has been claimed before, from a comparison of free ion states in titanium and other 3d transition metals (E. M. Shustorovich and M. E. Dyatkina, *Russ. J. Inorg. Chem.*, **4**, 251 (1959)). Experimentally, a singlet-triplet equilibrium has in fact been observed at room temperature in the complex $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}\cdot\text{bipyridine}$ (ref 4 and 5).

ently investigating these possibilities in more detail experimentally.

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Additions and Corrections

The Conformation of 1,4-Cyclohexadiene from Stereoisomeric Allylic-Allylic Proton Couplings [*J. Am. Chem. Soc.*, **90**, 3590 (1968)]. By E. W. GARBISCH, JR., and M. G. GRIFFITH, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.

The equation $\alpha \cong 180^\circ - \frac{1}{2}|60^\circ - \phi|$ is incorrect and should be replaced by $\alpha \cong 180^\circ - |60^\circ - \phi|$ [see D. J. Atkins and M. J. Perkins, *Tetrahedron Letters*, 2335 (1969)]. With this correction, $\alpha \cong 165^\circ$ rather than the reported value of 172° and is in qualitative agreement with the value of 159° determined by electron diffraction [H. Oberhammer and S. H. Bauer, *J. Am. Chem. Soc.*, **91**, 10 (1969)]. From the electron diffraction structure of 1,4-cyclohexadiene, the calculated value of ϕ is 41.3° which compares well with the value of 45° that was estimated from the allylic-allylic proton couplings.

Nuclear Magnetic Resonance Spectroscopy. Conformational Equilibria and Equilibration of 5,5-Difluoro-*cis*-hydrindan and 9-Methyl-5,5-difluoro-*cis*-hydrindan [*J. Am. Chem. Soc.*, **90**, 6997 (1968)]. By RUTH E. LACK and JOHN D. ROBERTS, Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.

Some of the labels on the curves in Figure 1 are incorrect. The correct temperatures and τ_1 values are (temp, $^\circ\text{C}$; τ , sec): $-46, 0.000075$; $-78, 0.00008$; $-92, 0.0004$; $-105, 0.0014$; $-123, 0.0185$. The other data and conclusions remain unchanged.

Mechanism of Secoiridoid Monoterpene Biosynthesis [*J. Am. Chem. Soc.*, **91**, 204 (1969)]. By ROCCO GUARNACCIA, LUIGI BOTTA, and CARMINE J. COSCIA, Department of Biochemistry, St. Louis University School of Medicine, St. Louis, Missouri 63104.

In Table I, the last entry in the column headed ^{14}C should be 1.16×10^4 rather than 1.16×10^6 .

Chemistry in Super Acids. III. Protonation of Alkanes and the Intermediacy of Alkanonium Ions, Pentacoordinated Carbon Cations of the CH_5^+ Type. Hydrogen Exchange, Protolytic Cleavage, Hydrogen Abstraction, and Polycondensation of Methane, Ethane, 2,2-Dimethylpropane (Neopentane), and 2,2,3,3-Tetramethyl-

butane in $\text{FSO}_3\text{H-SbF}_5$ ("Magic Acid") Solution [*J. Am. Chem. Soc.*, **91**, 3261 (1969)]. By GEORGE A. OLAH, GILLES KLOPMAN, and RICHARD H. SCHLOSBERG, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

On page 3264, column 2, the last five lines of text should have been placed between the fourth and fifth lines at the top of the same column.

Addition of a Functionalized Isoprene Unit to an Allyl Alcohol. I. The Synthesis of β -Sinensal and Related Topics [*J. Am. Chem. Soc.*, **91**, 3281 (1969)]. By ALAN F. THOMAS, Research Laboratories, Firmenich Cie, Geneva, Switzerland.

In Scheme III, page 3283, the numbers 16, 21, and 24 should be placed under the third column of formulas leading to 2-*trans*,6-*trans* and not under the fourth column.

The Anisotropy Factor of Optically Active Ketones [*J. Am. Chem. Soc.*, **91**, 3709 (1969)]. By GLEN M. ROBINSON and OSCAR E. WEIGANG, JR., Richardson Chemical Laboratories, Department of Chemistry, Tulane University, New Orleans, Louisiana 70118.

The three perspective drawings of Figure 1, page 3710, are incorrect in that they show axial substitutions rather than the equatorial substitutions which were the basis for measurements and calculations.

Stereochemistry of Polynuclear Compounds of the Main Group Elements. IX. Structure of Bis(dimethylamino)beryllium and Its Reaction with Trimethylaluminum [*J. Am. Chem. Soc.*, **91**, 4426 (1969)]. By J. L. ATWOOD and G. D. STUCKY, Department of Chemistry and Chemical Engineering and the Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801.

In the abstract, on line 6 the value of the b lattice parameter should read $14.073(8) \text{ \AA}$.

Syntheses via Dihydro-1,3-oxazines. VI. A Carboxyl Protecting Group Stable to the Grignard Reagent. A New Synthesis of Carboxylic Acids [*J. Am. Chem. Soc.*, **91**, 5886 (1969)]. By A. I. MEYERS, I. R. POLITZER,