

[5]Paracyclophane

Leonardus W. Jenneskens, Franciscus J. J. de Kanter,
Paulus A. Kraakman, Lucas A. M. Turkenburg,
Willem E. Koolhaas, Willem H. de Wolf, and
Friedrich Bickelhaupt*

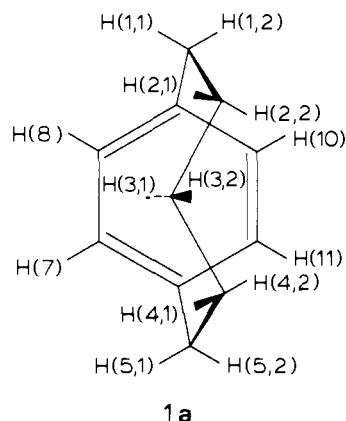
Vakgroep Organische Chemie, Vrije Universiteit
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Yoshito Tobe, Kiyomi Kakiuchi, and Yoshinobu Odaira

Department of Applied Fine Chemistry
Faculty of Engineering
Osaka University, Suita, Osaka 565, Japan

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[5]Paracyclophane (**1a**) is a molecule of considerable interest



from a theoretical point of view and a great challenge for experimental chemistry. The game of bending benzene rings by smaller and smaller bridges is fascinating and justified because it deepens our insight in that vague but useful concept of aromaticity, the strategy being to reach and define the point where aromaticity will break down due to excessive strain. The strain, however, will not only destabilize the molecule once it is formed, but will also tend to thwart conventional approaches toward its synthesis. Until this work, the available experimental evidence seemed to indicate that in the series of simple, homologous $[n]$ -paracyclophanes, the limit of stability had been reached at the stage of [6]paracyclophane (**1b**).¹⁻⁷ We have previously postulated the intermediacy of **1a** in the flow pyrolysis of the corresponding Dewar benzene **2a**,^{8,9} now, we present direct spectroscopic and chemical evidence for its photochemical formation at low temperature from **2a**.¹⁰

Irradiation of **2a**¹¹ in tetrahydrofuran-*d*₈ in a quartz NMR tube with a low-pressure mercury lamp at -60 °C yielded about 6-7% of **1a** after ca. 45 min. More prolonged irradiation did not increase the relative amount of **1a** but resulted in the formation of colorless insoluble polymeric material. The latter was also formed when **2a** was irradiated in *n*-hexane at 0 °C; after 40 min, new UV bands at 280 and 330 nm had reached a maximum value which gradually disappeared on longer irradiation.^{13,14}

The new UV spectrum is characteristic for a bent but aromatic benzene ring; the strong bathochromic shift is in good agreement with predictions from MM and VESCF calculations by Allinger et al.⁵ Unequivocal evidence for the structure assignment of **1a** was derived from the variable-temperature ¹H NMR spectrum at 250 MHz (THF-*d*₈).¹¹ It reveals the predicted⁵⁻⁷ C_s symmetry.¹⁴ At -72 °C, an AA'XX' pattern ($\delta(A)$ 7.44, $\delta(X)$ 7.38, ⁴J(A,X) = 1.1 Hz, ⁵J(A,X') = ca. 0 Hz) is observed for the aromatic protons; similarly, the two pairs of benzylic protons (H(1,1), H(5,1) and H(1,2), H(5,2), respectively) are in remarkably different environments. Most characteristic for a cyclophane structure are the high-field multiplets of two homobenzylic protons (H(2,2), H(4,2), δ 0.22) and one proton (H(3,1), δ 0.01) of the central methylene group. These high-field shifts are caused by the shielding effect of the aromatic ring. They occur at somewhat lower field than those of the shielded protons of **1b** (δ -0.62); it is not yet clear whether this difference is due to a slightly diminished ring current in **1a** or to a less favorable location within the shielding cone. In this context, it is of interest that the aromatic protons of **1a** resonate at lower field than expected, whereas a reduced ring current would lead to an upfield shift.

In agreement with intuition and with MM calculations,⁵ the thermodynamic and kinetic stability of **1a** is strongly reduced compared to **1b**. On warming the THF-*d*₈ solution to 0 °C, the signals of **1a** coalesce; line-shape analysis furnished $\Delta H^\ddagger = 13.7$ kcal mol⁻¹ and $\Delta S^\ddagger = -2.7$ cal mol⁻¹ deg⁻¹ for the flipping of the bridge. The strain in the bridge is higher in **1a** than in **2a**, as indicated by the lower flipping barrier in the latter (at $T = -49$ °C, $\Delta G^\ddagger(\mathbf{1a}) = 14.3$ kcal mol⁻¹; $\Delta G^\ddagger(\mathbf{2a}) = 11.7$ kcal mol⁻¹). The dynamic phenomena were reversible up to 0 °C, but at room temperature the signals of **1a** disappeared irreversibly. The products of this thermal decomposition have not yet been identified; the ortho isomer benzocycloheptene (**3a**) is formed for less than 0.1% of the **1a** originally present. In contrast, **3a** is formed instantaneously and quantitatively from **1a** at ca. -20 °C on addition of trifluoroacetic acid-*d* to the irradiated THF-*d*₈ solution; **2a** is unaffected. This is reminiscent of the similar behavior of **1b**, which rearranged to benzocyclooctene (**3b**) on acid treatment; however, the rearrangement of **1b** requires a higher temperature

(11) **1a**: ¹H NMR (250 MHz, THF-*d*₈)¹⁵ ($T = -72$ °C), δ 7.44 (d, ⁴J = 1.1 Hz, 2 H, H(7), H(8)), 7.38 (d, ⁴J = 1.1 Hz, 2 H, H(10), H(11)), 2.77 (ddd, ²J = 12.3, ³J = 5.9, ³J = 1.7 Hz, 2 H, H(1,2), H(5,2)), 2.11 (ddd, ²J = 12.3, ³J = 12.1, ³J = 5.1 Hz, 2 H, H(1,1), H(5,1)), 0.22 (dddd, ²J = 12.8, ³J = 12.1, ³J = 7.6, ³J = 5.9, ³J = ca. 1.5 Hz, 2 H, H(2,2), H(4,2)), 0.01 (dtt, ²J = 16.0, ³J = 7.6, ³J = 1.3 Hz, 1 H, H(3,1)); H(2,1), H(3,2) and H(4,1) are concealed under multiplets of **2a**; decoupling experiments indicate their chemical shift to be approximately δ 1.6. At $T = 0$ °C, H(7), H(8), H(10), and H(11) have coalesced at δ 7.41, -**2a** (numbering as in **1a**): ¹H NMR (250 MHz, THF-*d*₈)¹⁵ ($T = -72$ °C) δ 6.54 (s, 2 H, H(7), H(8)), 6.51 (s, 2 H, H(10), H(11)), 2.20 (dddd, ²J = 14.3, ³J = 6.1, ³J = 1.6, ⁴J = 1.6 Hz, 2 H, H(1,2), H(5,2)), 1.94 (dttt, ²J = 14.3, ³J = 12.3, ³J = 2.3, ⁴J = 1.6 Hz, 1 H, H(3,1)), 1.67 (ddd, ²J = 14.3, ³J = 12.4, ³J = 1.7 Hz, 2 H, H(1,1), H(5,1)), 1.63 (dddd, ²J = 14.4, ³J = 12.7, ³J = 6.1, ³J = 2.3, ³J = 1.7 Hz, 2 H, H(2,1), H(4,1)), 1.43 (dddd, ²J = 14.4, ³J = 12.4, ³J = 12.3, ³J = 2.2, ³J = 1.6 Hz, 2 H, H(2,2), H(4,2)), 1.10 ppm (dtt, ²J = 14.3, ³J = 12.7, ³J = 2.2 Hz, 1 H, H(3,2)). At $T = -49$ °C, δ 6.53 (s, 4 H); the other signals show broadening due to beginning coalescence.

(12) The yields were estimated by comparing integrals of corresponding proton signals of **1a** and **2a** and by assuming $\epsilon(330 \text{ nm})$ 600 in analogy to $\epsilon(296 \text{ nm})$ 600 for **1b** in *n*-hexane.

(13) Irradiation of **2a** in a matrix of 3-methylpentane also gave rise to an absorption maximum at 330 nm; preliminary results by J. W. Hofstra and G. P. Hoorneweg, personal communication.

(14) On irradiation of the 2-carbomethoxy derivative of **2a**, a UV maximum was observed at 360 nm; it is ascribed to 7-carbomethoxy[5]paracyclophane. Tobe, Y.; Kakiuchi, K.; Odaira, Y., unpublished results.

(15) At present, the assignment of chemical shifts of H(7), H(8) and H(10), H(11) is tentative and may have to be reversed after a full conformational analysis.

(1) Kane, V. V.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2643.

(2) Kammula, S. L.; Iroff, L. D.; Jones, M., Jr.; Van Straten, J. W.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1977**, *99*, 5815.

(3) (a) Liebe, J.; Wolff, C.; Tochtermann, W. *Tetrahedron Lett.* **1982**, *23*, 171. (b) Wolff, C.; Liebe, J.; Tochtermann, W. *Tetrahedron Lett.* **1982**, *23*, 1143.

(4) (a) Tobe, Y.; Kakiuchi, K.; Odaira, Y.; Hosaki, T.; Kai, Y.; Kasai, N. *J. Am. Chem. Soc.* **1983**, *105*, 1376. (b) Tobe, Y.; Ueda, K.; Kakiuchi, K.; Odaira, Y. *Chem. Lett.* **1983**, 1645.

(5) Allinger, N. L.; Sprague, J. T.; Liljefors, T. *J. Am. Chem. Soc.* **1974**, *96*, 5100.

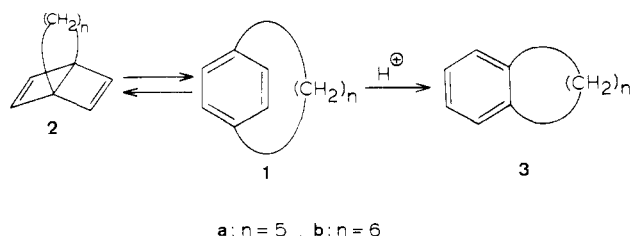
(6) (a) Schmidt, H.; Schweig, A.; Thiel, W.; Jones, M., Jr. *Chem. Ber.* **1978**, *111*, 1958. (b) Gleiter, R.; Hopf, H.; Eckert-Maksic, M.; Noble, K. L. *Chem. Ber.* **1980**, *113*, 3401.

(7) Carballeira, L.; Casado, J.; González, E.; Ríos, M. A. *J. Chem. Phys.* **1982**, *77*, 5655.

(8) Van Straten, J. W.; Landheer, I. J.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1975**, 4499.

(9) Van Straten, J. W.; Turkenburg, L. A. M.; De Wolf, W. H.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 89.

(10) Preliminary, but not unequivocal, results were presented by: Turkenburg, L. A. M. Thesis Vrije Universiteit, Amsterdam, 1982.



and gives some [6]metacyclophane as a byproduct.^{4b} The rearrangement of **1a** to **3a** furnishes a chemical corroboration of the nature and the composition of **1a**.

One of the most fascinating conclusions is that the benzene ring retains its aromatic character with remarkable tenacity, in contrast to predictions based on theoretical calculations.^{6a,7} The UV and especially the ¹H NMR spectra reveal an essentially delocalized, aromatic structure; the molecule does, however, pay a toll to strain in giving up another property traditionally connected with benzene-like aromaticity, i.e., stability.

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Registry No. **1a**, 58634-37-0; **2a**, 53600-57-0; **3a**, 1075-16-7.

Acetylene Derivatives of Titanocene[†]

Helmut G. Alt* and Heidi E. Engelhardt

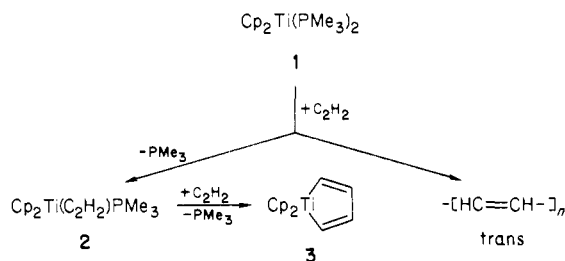
Laboratorium für Anorganische Chemie
Universität Bayreuth, D-8580 Bayreuth, FRG

Marvin D. Rausch* and Lawrence B. Kool

Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01003
Received January 21, 1985

Acetylene complexes of titanium have been proposed as key intermediates in the formation of polyacetylene [CH]_x.¹ At the present time, however, in spite of many attempts, no C₂H₂ derivatives of a group 4 transition metal could be prepared. The reason for this failure is the increased reactivity of the C₂H₂ hydrogens induced by the coordination of the alkyne to the metal. We now report evidence for the first C₂H₂ complex of titanocene and the first unsubstituted metallacyclopentadiene containing an early transition metal.

The highly reactive "titanocene" source Cp₂Ti(PMe₃)₂ (**1**) (Cp = η⁵-cyclopentadienyl, Me = methyl)² reacts instantly with C₂H₂ in solution forming Cp₂Ti(C₂H₂)PMe₃ (**2**), the metallacycle Cp₂TiC₄H₄ (**3**), polyacetylene, and traces of benzene.



[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(1) Chien, J.C.W. "Polyacetylene: Chemistry, Physics and Material Science", Academic Press: New York, 1984.

(2) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem.*, in press; *Angew. Chem., Int. Ed. Engl.*, in press.

In a typical reaction to generate and characterize **2** in solution, 33.0 mg (0.1 mmol) of **1** were dissolved in 0.4 mL of cyclohexane-*d*₁₂ and treated with the stoichiometric amount of C₂H₂ at 10 °C. The red-brown solution immediately turned purple with the formation of **2**. The ¹H NMR spectrum of **2** exhibits two broad doublets for the C₂H₂ ligand, resulting from coupling of the two nonequivalent C₂H₂ protons with the ³¹P nucleus of the PMe₃ ligand [δ 8.82 (*J* = 9.0 Hz) and 6.99 (*J* = 5.4 Hz)], as confirmed by the ³¹P-decoupled ¹H NMR spectrum.³ These results imply a configuration in which the CC axis of the C₂H₂ ligand lies in the symmetry plane of a pseudotetrahedral molecule, analogous to that shown for Cp₂Ti(C₂Ph₂)CO⁴ and Cp₂Ta(C₂H₄)H⁵ (Figure 1). In the IR spectrum of **2**, a band is observed at 1618 cm⁻¹ (cyclohexane) that is indicative of a C-C double bond.⁶

On the basis of these spectroscopic data and in view of the absence of a C₂H₂ ligand rotation we formulate **2** as a titanacyclopropene derivative. This conclusion is supported by the reaction of **2** with hydrogen chloride, which yields ethylene and Cp₂TiCl₂. All attempts to isolate **2** as a solid have so far been unsuccessful. Removal of the solvent in vacuo yields a dark purple paramagnetic residue that is not identical with **2**.

Metallacycle **3** was obtained in a reaction of 2 mmol (0.66 g) of **1** in 20 mL of toluene with an excess of C₂H₂. Filtration of the resulting suspension, removal of the solvent in vacuo, and recrystallization of the residue from pentane afforded **3** as a light brown, relatively air- and light-sensitive powder.⁷ In the ¹H NMR spectrum of **3** (CDCl₃, 20 °C), a sharp singlet can be observed for the Cp ligands at 6.18 ppm and an AA'BB' pattern for the four protons of the metallacyclic ring in the α- and β-positions (δ 6.30 (m) and 5.63 (m), respectively). These chemical shifts are consistent with the only other known C₄H₄ metallacycle, CpCo(PMe₃)C₄H₄.⁸ In the ¹³C NMR spectrum of **3** (CDCl₃, 20 °C), the Cp rings give rise to one signal at δ 113.0. The carbon atoms of the C₄H₄ moiety directly bonded to the metal are more strongly deshielded (198.5 ppm) than are the carbon atoms in the β-position (124.8 ppm).⁹ This assignment is also supported by the different ²J(C,H) long-range couplings of C_α and C_β.

In the mass spectrum of **3**, the molecular ion (*m/z* 230) is observed, as well as peaks derived from the fragmentation of this ion. The IR spectrum of **3** exhibits a ν(C=C) band at 1442 cm⁻¹ (KBr), indicative of an olefinic double bond. The metallacyclic character of **3** is further established by its reaction with hydrogen chloride at -60 °C to yield mainly 1,3-butadiene and Cp₂TiCl₂, as identified by their ¹H and ¹³C NMR spectra. The latter complex is also formed when chloroform solutions of **3** are kept at room temperature for a period of several days.

The insoluble black residue from the reaction of **1** and an excess of C₂H₂ shows IR bands characteristic for *trans*-polyacetylene.¹ Elemental analysis¹⁰ of this material prepared under argon con-

(3) Other chemical shifts of **2**: ¹H NMR δ 5.25 (Cp), 1.09 (br, PMe₃); ³¹P NMR 28.1 ppm.

(4) Fachinetti, G.; Floriani, C.; Marchetti, F.; Mellini, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1398.

(5) Eichner, M. E.; Alt, H. G.; Rausch, M. D. *J. Organomet. Chem.* **1984**, 264, 309.

(6) By comparison, the C=C stretching frequency for the metallacyclopropene complex Cp₂MoC₂H₂ is observed at 1613 cm⁻¹. (a) Tang Wong, K. L.; Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1974**, 96, 3694. (b) Thomas, J. L. *Inorg. Chem.* **1978**, 17, 1507.

(7) **3**: yield 250 mg, 55%; >45 °C dec. Anal. Calcd for C₁₄H₁₄Ti: C, 73.06; H, 6.13. Found: C, 71.31; H, 7.24. The reduction of Cp₂TiCl₂ with sodium in C₂H₂ atmosphere in toluene did not yield **3** but rather polyacetylene.

(8) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1984**, 272, 251.

(9) These conclusions are consistent with earlier studies on tetrasubstituted metallacyclopentadienes: Mattia, J.; Sikora, D. J.; Macomber, D. W.; Rausch, M. D.; Hickey, J. P.; Friesen, G. D.; Todd, L. J. *J. Organomet. Chem.* **1981**, 213, 441.