is not observed at 600 ps, it may be implied that $k_2/k_{-2} > 10$.[17] The biradical decays either by heterolytic cleavage, k_3, yielding a solvent-separated ion pair, or by intersystem crossing, k_4, followed by β-scission, k_β, and ring closure k_c, presumable with $k_c + k_\beta > k_4$. As the spin state of the ion pair is a triplet, decay to the reactants by electron transfer will not occur on the picosecond timescale.[10] With the 20% estimated yield of anion formation and the rate of decay of the biradical, $k_d = 6.3 \times 10^8$ s^{-1}, then $k_3 = 1.3\ 10^8$ s^{-1} and $k_4 = 5.0 \times 10^8$ s^{-1}.

The lifetime of the 1,4-biradical observed in this study is shorter than that of previously studied biradicals.[11,20] The rate of decay of the biradical intermediate formed in the photocycloaddition of benzophenone and dioxene, $k_d = 6.3 \times 10^8$ s^{-1}, is substantially greater than that found[11] for the 1,4-biradical generated by Norrish Type II reaction of valerophenone, $k_d = 1.4 \times 10^7$ s^{-1}. If the lifetime of both biradicals is determined by the rate of intersystem crossing then the increase in rate by a factor of 45 may reflect that for the benzophenone–dioxene derived biradical there is (1) a larger spin–orbit coupling[18] resulting from radical interaction with oxygen and/or (2) a smaller singlet–triplet splitting resulting from greater electron delocalization over the additional phenyl substituent.[19,20] Again it is noted that the biradical derived from photocycloaddition has an alternative decay pathway, namely, heterolytic cleavage, which is independent of the biradical spin state.

Acknowledgment. This research is supported by a grant from NIH (EYO 2922-02) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank John Hubbs for providing samples of dioxene.

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(17) Based upon the sensitivity of the instrument.

(18) Kaptein, R.; DeKanter, F. J.; Rist, G. *J. Chem. Soc., Chem. Commun.* **1981**, 499.

(19) Stephenson, L. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1971**, *93*, 1968.

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Reaction of Bicyclo[1.1.0]butanes with Pt(II) Complexes. Isolation and Characterization of New Platinacycle Compounds

Akira Miyashita, Mikio Takahashi,† and Hidemasa Takaya*

Chemical Materials Center, Institute for Molecular Science
Okazaki National Research Institutes
Myodaiji, Okazaki 444, Japan

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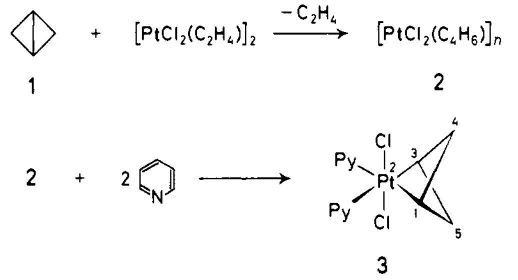
Transition-metal-catalyzed isomerization of strained cyclic hydrocarbons has been a subject of recent interest.[1] Bicyclo[1.1.0]butane (**1**), the smallest bicyclic hydrocarbon, and its derivatives are the molecules which have been studied most extensively. Compound **1** is rather thermally stable, but it suffers from facile rearrangements mainly into 1,3-dienes by a variety of transition-metal catalysts.[1-3] Although much effort has been directed toward the elucidation of the mechanism of catalysis,[4] numerous questions still remain to be answered: (1) how does **1** interact with the metal complexes prior to carbon–carbon bond cleavage, (2) is the intermediate a metallacyclobutane-type or a complex in which the strained C–C bond remains intact, and so on. In order to get more insight into the mechanism of the transition-metal catalyzed reactions of **1**, we have studied the reactions of **1** with Pt(II) complexes. In this paper we describe the first isolation of transition-metal complexes of **1** and their unique chemical behavior.

Table I. Thermal Decomposition of **3**

dec condition		product composition, %[a]				
solvent	temp, °C					
	190[b]	20	18	60	0	2
CH_2Cl_2	20[c]	31	40	17	12	0

[a] All products were isolated by preparative gas chromatography [GC Durapak (octane on Porasil C) treated with trimethylsilyl ester of *N*-(trimethylsilyl)ethanimidic acid, 40 °C] and identified by the comparison of mass, ^1H, and ^{13}C NMR spectra, and retention times of gas chromatography with those of authentic samples. [b] Pyrolysis of solid was performed under vacuum, and products were collected on a cold finger cooled with liquid N_2. Temperature was raised from 20 °C to the specified point at a rate of 5 °C/min. [c] The solution was stirred at 20 °C for 12 h.

Treatment of **1** with a catalytic amount of Zeise's dimer, $[PtCl_2(C_2H_4)]_2$, in acetone at 23 °C for 20 min under argon afforded butadiene in quantitative yield. When this reaction was carried out at −45 °C for 48 h, a 1:1 complex, $[PtCl_2(C_4H_6)]_n$ (**2**), was obtained as yellow-orange crystalline material in 97% yield, mp 60 °C dec. The insolubility of complex **2** in most common organic solvents made structural elucidation difficult.[5] Further treatment of a suspension of **2** in CH_2Cl_2 at −50 °C with 2 equiv of pyridine resulted in the formation of a yellow solution from which 2-[bis(pyridine)dichloroplatina]bicyclo[1.1.1]pentane (**3**) (Py = pyridine) was isolated as white fine crystals in 94% yield. The pure sample of **3** was obtained by column chromatography on Florisil (1:50 C_2H_5OH–CH_2Cl_2) at −60 °C in 57% yield,[6] mp 160–162 °C dec. The isolated **3** is relatively stable at room temperature, but in solution it slowly decomposes even at −25 °C.



The structural assignments of **3** were done on the basis of the spectral data. Only one platinum–halogen stretching vibration was observed at 320 cm^{-1}, which is consistent with the trans-halogen structure.[7,8] The proton-decoupled ^{13}C NMR spectrum of **3** (−35 °C, $^{12}CD_2Cl_2$) exhibited only two kinds of signals for the four aliphatic carbons centered at δ 19.7 (a broad signal accompanied by platinum satellites, $J_{Pt-C} = 621$ Hz, C_1 and C_3)

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† Research Student, Department of Chemistry, Faculty of Science, Nagoya University, April 1979–March 1981.

(1) For a review, see: (a) Paquette, L. A. *Acc. Chem. Res.* **1971**, *4*, 280–287. (b) Mango, F. D. *Coord. Chem. Rev.* **1975**, *15*, 109–205. (c) Bishop, K. C., III. *Chem. Rev.* **1976**, 461–486. (d) Halpern, J. In "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. II, pp 705–730.

(2) (a) Galantay, E.; Paolella, N.; Barcza, S.; Coombs, R. V.; Weber, H. P. *J. Am. Chem. Soc.* **1970**, *92*, 5771–5773. (b) Paquette, L. A.; Zon, G. *Ibid.* **1974**, *96*, 224–233. (c) Sakai, M.; Westberg, H. H.; Yamaguchi, H.; Masamune, S. *Ibid.* **1971**, *93*, 4611–4613. (d) Gassman, P. G.; Reitz, R. R. *Ibid.* **1973**, *95*, 3057–3058. (e) Murata, I.; Nakasuji, K. *Tetrahedron Lett.* **1973**, 47–50. (f) Moriarty, R. M.; Chen, K.-N.; Flippen, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 6489–6490 and references cited therein.

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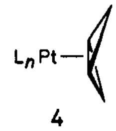
(5) Infrared (IR) spectrum of **2** (KBr pellet): 2920 (m), 2850 (sh), 1430 (w), 1223 (s), 1090 (w), and 840 cm^{-1} (w). The thermal decomposition of **2** in vacuo at 80 °C produced the starting bicyclobutane **1** and butadiene in a ratio of 44:56.

(6) The C, H, and N analyses of **3** were satisfactory.

0002-7863/81/1503-6257$01.25/0

and 45.6 (a broad singlet, C_4 and C_5) in addition to those of the coordinated pyridines (δ 126.0, 139.3, and 151.0).[9] The gated-decoupled spectrum of 3 has δ 19.7 (doublet, J_{C-H} = 157 Hz) and 45.6 (triplet, J_{C-H} = 143 Hz). The above coupling constants are in contrast with those of cyclopropane (J_{C-H} = 162 Hz), the starting hydrocarbon **1** (J_{C_1-H} = 205 Hz, $J_{C_2-H_{endo}}$ = 170 Hz, and $J_{C_2-H_{exo}}$ = 152 Hz), and cyclobutane (J_{C-H} = 136 Hz). Substitution of the two angular protons of **1** with deuteriums resulted in considerably lower intensities of the signal at δ 19.7 and of its platinum satellites due to the loss of the nuclear Overhauser effect, which shows that no scrambling either of carbon or hydrogen atoms took place. The ^{195}Pt NMR spectrum of **3** (−60 °C, CD_2Cl_2) showed only a singlet at 214.1 ppm upfield from the external K_2PtCl_4 standard.[10] The aliphatic group in **3** was not displaced by added tertiary phosphines, carbon monoxide, or 1,3-dideuteriobicyclo[1.1.0]butane in CH_2Cl_2 at −35 °C. These results are consistent with the assigned structure of 3, and structure **4** (L = pyridine and chloride) in which **1** coordinates to Pt(II) in edge-on manner[12] was ruled out.



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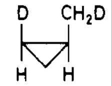
The thermal decomposition of **3** was carried out, and the results were summarized in Table I. Unexpectedly, significant amount of **1** was regenerated. Reductive elimination of the aliphatic group would produce the starting **1**,[13,14] while β-hydrogen elimination process affords cyclobutene. The direct isomerization of **1** catalyzed by **3** at 23 °C in CH_2Cl_2 proceeded rather slowly to give butadiene (79%), cyclobutene (20%), and 3-methylcyclopropene (1%)[16] (30 h, 21% conversion).[17] This similarity of products between thermal decomposition of **3** and catalysis strongly suggests that **3** is an important intermediate in the isomerization of **1**. Straightforward interpretation of the formation of 3-methylcyclopropene and methylenecyclopropane on thermolysis of **3**, though in low yields, appears to be difficult at this stage (vide infra).

Table II. Temperature Dependence of Proton-Decoupled ^{13}C and ^{195}Pt NMR Spectra of **3**[a]

	^{13}C chem shift, ppm[b] ($\Delta\nu_{1/2}$,[c] Hz)		^{195}Pt chem shift, ppm[d] ($\Delta\nu_{1/2}$,[c] Hz)
temp, °C	C_1 and C_3	C_4 and C_5	
−12	19.9 (14)	46.4 (14)	
−45	19.7 (26)	46.1 (27)	−210.7 (40)
−60	19.4 (43)	45.6 (43)	−214.1 (55)
−88	18.6 (80)	44.9 (88)	−219.4 (91)
−106[e]	f	f	

[a] All spectra were taken in $^{12}CD_2Cl_2$ unless otherwise stated. [b] Chemical shifts were calculated on the basis of the signal due to CD_2Cl_2 (δ 55.0). [c] Line width at half-height. [d] Chemical shifts were obtained from external K_2PtCl_4 in D_2O. [e] Measured in a mixture of CF_2Cl_2 and CD_2Cl_2 (15:85). [f] Chemical shift and line width at half-height could not be determined because of a very broad signal.

Reduction of **3** with $LiAlD_4$ in THF below −20 °C produced *cis*-1-deuteriomethyl-2-deuteriocyclopropane (**5**, 30% yield)[18] and 1,3-dideuteriocyclobutane (**6**, 11%)[18] in addition to **1** (53%) and butadiene (3%) The production of **5** indicates an intervention of another complex of type **7**. The formation of 1-methylcyclopropene and methylenecyclopropane in the thermolysis of **3** can also be explained by β-hydrogen elimination processes involving the complex **7**. These findings suggest that the two complexes **3** and **7** might be in rapid equilibrium in solution. In fact, we observed remarkable temperature dependence of the NMR spectra of **3** in solution. Apparent line broadening in the ^{13}C and ^{195}Pt NMR spectra was observed at low temperature as shown in Table II. Although the fluxional behavior of the complex **3** was not frozen out even at −106 °C, the line broadening in the NMR spectra indicates that **3** is in rapid equilibrium with another complex, most probably with **7**. The complex **7** will be converted to **8** by way of **3**. Such rapid equilibrium will make C_1 and C_3 and C_4 and C_5 respectively, magnetically equivalent. Because of the rapid motion of the aliphatic group, the coupling constants become averaged so that, we believe, the equilibrium in eq 1 lies largely on the side of **3**. This would account for the observed platinum–carbon coupling constant for the methine carbons (J_{Pt-C} = 621 Hz) and a small value (<150 Hz, if any) for that of the methylene carbons which might be covered up under the apron of the broad methylene signal at 46.4 ppm.



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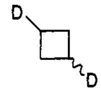

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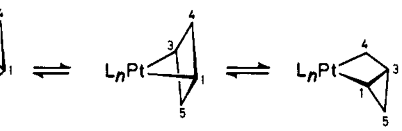

7 3 8 (1)

Compound **3** can be considered to arise from the initial interaction of the central carbon–carbon bond of **1** which has eminent π character[19] with Pt(II) species followed by oxidative addition of this bond to the metal.[20] An alternative pathway which involves an initial formation of **7** and **8** followed by rearrangements of these complexes to **3**, however, cannot be ruled out, although the interaction of one of the side bonds of **1** with platinum, which would be requisite for the direct formation of **7** and **8** from **1** and Pt(II) species, is unfavorable on the basis of molecular orbital (MO) considerations.[3,19a,c,21]

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(7) IR spectrum of **3** (KBr pellet): 3080 (w), 2910 (m), 2860 (sh), 1590 (s), 1480 (w), 1440 (s), 1230 (sh), 1220 (vs), 1140 (s), 1060 (m), 1040 (w), 1000 (m), 850 (s), 750 (s), 690 (s), 630 (m), and 320 cm^{-1} (w).

(8) Binns, S. E.; Cragg, R. H.; Gillard, R. D.; Heaton, B. T. Pilbrow, M. F. *J. Chem. Soc. A* **1969**, 1227–1231.

(9) The ^{1}H NMR spectrum of **3** unexpectedly showed poorly resolved broad signals due to the aliphatic protons in the region δ 0.1–3.4 with the temperature ranging from −80 to −35 °C.

(10) Tipper's complex, [bis(pyridine)dichloroplatina]cyclobutane,[11] exhibited a sharp singlet at 429.8 ppm downfield from the signal due to **3**. No conclusions on the oxidation state of platinum **3**, however, can be drawn due to the lack of general informations on ^{195}Pt chemical shifts of organoplatinum compounds.

(11) Al-Essa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Am. Chem. Soc.* **1979**, *101*, 364–370.

(12) (a) Tipper, C. F. H. *J. Chem. Soc.* **1955**, 2045–2046. (b) Irwin, W. J.; McQuillin, F. J. *Tetrahedron Lett.* **1968**, 1937–1940. (c) Volger, H. C.; Hogeveen, H.; Gaasbeek, M. M. P. *J. Am. Chem. Soc.* **1969**, *91*, 218–219, 2137–2138. (d) Katz, T. J.; Cerefice, S. *Ibid.* **1969**, *91*, 2405–2406.

(13) Reductive elimination of cyclopropanes from platinacyclobutanes has been well-known: Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725. See also ref 11.

(14) It is conceivable that **1** resulted from an intramolecular carbene addition of the allylcarbene–platinum complex which might be formed by a rearrangement of **3**,[4] but such types of carbene–metal complexes tend to suffer from 1,2-hydrogen shift to give 1,3-dienes as major products.[15]

(15) Kirmse, W. In "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971; Chapter 12.

(16) Köster, R.; Arora, S.; Binger, P. *Liebigs Ann. Chem.* **1973**, 1219–1235.

(17) Cyclobutene was further consumed in the catalytic system, and the yield varied depending on the reaction conditions. The details will be described elsewhere.

(18) The compounds **5** and **6** were isolated by preparative gas chromatography [GC Durapak (octane on Porasil C) treated with trimethylsilyl ester of *N*-(trimethylsilyl)ethanimidic acid, 40 °C]. The structures of these products were determined by the comparison of their ^{1}H and ^{13}C NMR spectra and mass spectral cracking patterns with those of undeuterated compounds.

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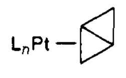
The question of mechanism of the interconversion between the center-opened type complex **3** and the side-opened type **7** remains to be answered. The lack of ligand exchange reactions is against the process in which the edge-on complexes **4** and **9** are important transient intermediates. Moreover, as described above, MO



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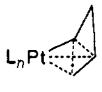

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considerations suggest that the formation of **9** is energetically unfavorable. Thus, we think that an intramolecular concerted process via a transition state like **10** is most probable.[22] This type of rearrangement is formally related to the cyclobutyl–cyclopropylcarbinyl interconversions which have been well-documented in carbonium ion chemistry.[23]

Acknowledgment. We are grateful to Professors J. Halpern (University of Chicago), R. Noyori (Nagoya University), and R. Pettit (University of Texas, Austin) for helpful discussions. We thank the Ministry of Education, Japan, for partial support of this research (Grant 574206).

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(21) Jorgensen, W. L.; Salem, L. In "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973; pp 203–205.

(22) Such species could be stable complexes, and rapid interconversion among this kind of species also may explain our experimental findings.

(23) Staral, J. S.; Yavari, I., Roberts, J. D.; Surya Prakash, G. K.; Donovan, D. J.; Olah, G. A. *J. Am. Chem. Soc.* **1978**, *100*, 8016–8018 and references therein.

Mechanism of the Reppe Cyclooctatetraene Synthesis from Ethyne: A Labeling Experiment

Robert E. Colborn and K. Peter C. Vollhardt*,†

Department of Chemistry, University of California
and the Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

Received May 15, 1981

The mechanism of the remarkable nickel-catalyzed cyclotetramerization of ethyne discovered by Reppe[1] is little understood, despite the synthetic significance of the reaction[2] and the mechanistic curiosity it has generated.[3] Originally formulated as a concerted "zipper" process,[4] recent work has suggested the possibility of the occurrence of a stepwise topological equivalent possibly involving dinuclear metallacycles.[5] Particularly significant has been the discovery of metal-mediated alkyne-linking processes resulting in flyover bridges between two metal centers composed of four alkyne units[5f,g] and the detection of a remarkably facile reversible cyclooctatetraene (COT) ring-opening reaction.[5c,e]

Scheme I

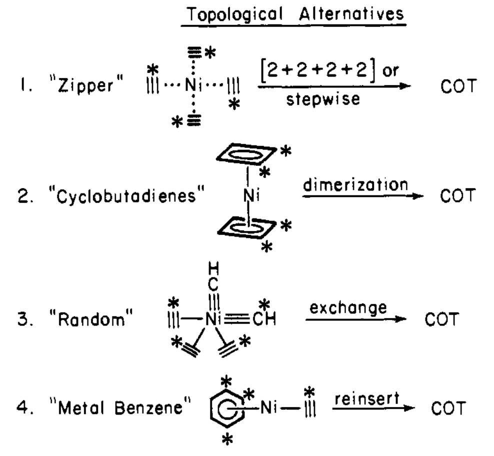

Table I. Theoretical Isomer Distribution of Labeled Cyclooctatetraenes According to Various Mechanisms of Formation

		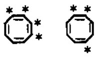	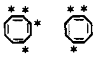	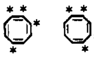				
zipper	0%	0%	0%	0%	50%	25%	12 5%	12.5%
cyclobutadiene	3.1	12.5	6.25	6.25	37.5	15.6	6.25	12.5
random	12.5	12.5	12 5	12.5	12.5	12 5	12.5	12.5
metal benzene	0	6.25	6.25	6.25	43 75	18.75	6.25	12.5

Table II. Calculated Relative Abundance of Labeled C_4 Fragments Derived From COT-$*C_4$

	zipper	cyclobutadiene	random	metal-benzene
$*C_4$	0.00	0.39	1.56	0.00
$C*C_3$	12.50	17.19	18.75	15.62
C_2*C_2	75.00	64.84	59.37	68.75
C_3*C	12.50	17.19	18.75	15.62
C_4	0.00	0.39	1.56	0.00

Other work has implicated the intermediacy of nickel–cyclobutadiene complexes.[6] Such intermediates were originally discounted as unlikely due to the stability of isolated representatives of this class of compounds.[7] Through the use of isotopic labeling they were also shown to be absent in a number of transition-metal-catalyzed alkyne cyclizations leading to aromatic compounds.[8] On the other hand, recently several cyclobutadiene–nickel complexes have been isolated which appear to be good models for potential intermediates in COT synthesis,[6] particularly some which may be decomposed to COT under mild conditions.[6b]

In addition to the "zipper-stepwise" (hereafter called "zipper") and the "cyclobutadiene" mechanisms, there are other major topological alternatives[9] (Scheme I): a "random" process in which

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† Camille and Henry Dreyfuss Teacher-Scholar, 1978–1983.

(1) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Liebigs Ann. Chem.*, **560**, 1 (1948).

(2) A. C. Cope and H. C. Campbell, *J. Am. Chem. Soc.*, 74, 179 (1952); A. C. Cope and D. S. Smith, *ibid.*, **74**, 5136 (1952); A. C. Cope and D. F. Rugen, *ibid.*, **75**, 3215 (1953); A. C. Cope and R. M. Pike, *ibid.*, **75**, 3220 (1953); J. R. Leto and M. F. Leto, *ibid.*, **83**, 2944 (1961); P. Chini, N. Palladino, and A. Santambrogio, *J. Chem. Soc. C* 836 (1967); G. A. Chukhadzhyan, E. L. Sarkisyan, and T. S. Elbakyan, *Zh. Obshch. Khim.*, **43**, 2302 (1973); V. K. Shitikov, T. N. Kolosova, V. A. Sergeev, V. V. Korshak, and P. O. Okulevich, *Zh. Org. Khim.*, **10**, 1007 (1974); L. H. Simons and J. J. Lagowski, *J. Org. Chem.*, **43**, 3247 (1978).

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