6 gives the base peak at m/z 274 and only a minor protonation contributes to m/z 275. A conversion of **6** to **7** on the emitter should also be recognizable from the fragmentation pattern and the best anode temperature. However, no other signals than those stated could be detected between m/z 141 and m/z 400, and the best anode temperature for **6** is 10 mA below that for **7**.

Elemental analysis was in agreement with the proposed chemical formula with two molecules of crystal water. Analysis by Röntgen diffraction was unsuccessful because of the instability of the crystalline product.

The reaction mechanism that leads to the formation of **6** is not fully clear. Takamizawa et al.[13] have proposed a mechanism for the formation of **3** in which cleavage of a primary ozonide was followed by cyclization of the resulting zwitterion fragment (cf. ref 13). We suggest that under our conditions, especially the slightly alkaline solution, cyclization occurs, preferably to yield **6**.

Compound **6** can be converted to **3**, possibly by reaction with its crystal water, by dissolving it in acetone/CH_2Cl_2 and refluxing the solution for 30 min. The yield of this reaction was ~70%. Refluxing for a longer period of time primarily resulted in the formation of **5**. Conversion of **6** into the stable isomer **7** was also noticed under these conditions. Direct preparation of **3** from the ozonolysis reaction mixture, by refluxing the CH_2Cl_2 extract together with the oil remaining from the freeze-dried aqueous phase, gave an overall yield of **3** of ~30% after crystallization from ether.

Since **6** can be converted to **3**, it is likely that the oxazirane group is cis to the phosphoryl oxygen, because it is known that the peroxide group of **3** also has the cis configuration.[14,15] A small amount of the trans isomer of **6** (less than 10%) may contaminate the isolated crystals since the ^1H NMR spectrum shows a small triplet at δ 5.42 ($J = 6$ Hz) next to the triplet at δ 5.25. Peter et al.[16] have observed that ozonation of **1** leads to the formation of **3**, **7**, and an unstable compound that was suggested to be the trans diastereomer of **3**. The described chromatographical and chemical behavior leads us to the suggestion that Peter et al. might also have observed **6**.

Compound **6** also exhibits cytostatic activity in vitro. On BHK cells, it has the same cytostatic action as **3** ($ED_{50} = 7$–10 μM when drugs are left in the medium for the full period of growth). On $3T3_f$ cells, the cytotoxic capacity of **6** is even a little stronger in comparison with **3** (**6**, $ED_{90} = 9$ μM; **3**, $ED_{90} = 17$ μM; drug treatment, 1 h).

(13) Takamizawa, A.; Matsumoto, S.; Iwata, T.; Tochino, Y.; Katagiri, K.; Yamaguchi, K.; Shiratori, O. *J. Med. Chem.* **1975,** *18,* 376–383.

(14) Camerman, A.; Smith, H. W.; Camerman, N. *Biochem. Biophys. Res. Commun.* **1975,** *65,* 828–832.

(15) Camerman, A.; Smith, H. W.; Camerman, N. *Cancer Treat. Rep.* **1976,** *60,* 517–522.

(16) Peter, G.; Wagner, T.; Hohorst, H.-J. *Cancer Treat. Rep.* **1976,** *60,* 429–435.

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Flow Pyrolysis and Direct and SiF₄-Sensitized Laser-Induced Decomposition of Tetralin. Identification of Retro-[2 + 4] Cleavage as the Primary Homogeneous Thermal Decomposition Channel

Sir:

The thermal chemistry of tetralin (**1**) has been under intense investigation recently,[1] due to interest in the fate of hydrogen donors which are used as recycle liquids in the solvent refining of coal. The reactivity of tetralin appears to be dependent on the presence of hydrogen, hydrogen-acceptor molecules, different types of reactor surfaces, and surface history. This has resulted in conflicting data[2] in the literature and confusion as to what the thermal reactivity is in the absence of any catalytic effects. In an effort to resolve this situation, we report the reactivity of tetralin resulting from several different methods of activation.

Three methods for energization of **1** were investigated: conventional flow pyrolysis, infrared multiphoton excitation, and sensitized infrared laser thermal activation. All three give rise to six major products: benzocyclobutene (**2**), styrene (**3**), *o*-allyltoluene (**4**), indene (**5**), 1,2-dihydronaphthalene (**6**), and naphthalene (**7**) (see Scheme I), and several minor products.[3] The primary concern of this work is to delineate the energetics of the ethylene-loss channel (giving rise to **2** and **3**) vs. the hydrogen-loss channel (giving rise to **6** and **7**) without interference from catalytic effects.

A number of parameters affected the product distribution for the decomposition in a flow reactor,[4] including the composition of the surface, the history of the surface, and the pressure of the system (see Table I). However, except at the lowest pressure, where the two reaction channels became comparable, dehydrogenation was always the predominant decomposition mode. Unconditioned surfaces, higher pressures, and longer contact times in the reactor led to more dehydrogenation of **1**.

Multiphoton excitation of **1** in the gas phase was accomplished[5] with a pulsed CO_2 TEA laser[6,7] tuned to 945.99 cm^{-1}. All six major products[8] found from the pyrolysis also resulted from photolysis of tetralin, including one additional product, phenylacetylene.[8] The distribution of these products, however, was at variance with the distribution from the pyrolysis (see Table I); the major reaction channel for the multiphoton dissociation of tetralin involved ethylene loss.

In the third method of activation, **1** and varying pressures of SiF₄, an inert sensitizer[10] which absorbs strongly in the infrared,

(1) (a) A. G. Loudon, A. Maccoll, and S. K. Wong, *J. Chem. Soc. B,* 1733 (1970); (b) R. J. Hooper, H. A. J. Battaerd, and D. G. Evans, *Fuel,* **58,** 132 (1979); (c) P. Bredael and T. H. Vinh, *ibid.,* **58,** 211 (1979); (d) B. M. Benjamin, E. W. Hagaman, V. F. Raaen, and C. J. Collins, *ibid.,* **58,** 386 (1979); (e) T. Gangwer, D. MacKenize, and S. Casano, *J. Phys. Chem.,* **83,** 2013 (1979).

(2) For example, compare ref 1a and 1e for the static pyrolysis results.

(3) The minor products have been tentatively identified as toluene, ethylbenzene, 1,4-dihydronaphthalene, and *o*-ethylstyrene. Traces of other unidentified aromatics were also observed. In nearly all experiments, none of the above products amounted to more than 1% of the total reaction mixture.

(4) For a description of the flow reactor, see: M. D'Amore, R. G. Bergman, M. Kent, and E. Hedaya, *J. Chem. Soc., Chem. Commun.,* 49 (1972).

(5) A sample cell consisted of a 2-cm i.d. by 20-cm long Pyrex cell with KCl windows mounted at the Brewster angle. The cell was pumped to $<10^{-5}$ torr on a grease-free vacuum line and was pressured to 0.325 torr of **1** for all photolysis experiments. Pressures of all gases were measured with a capacitance manometer.

(6) The laser pulse consisted of a 100-ns pulse followed by a 1-μs tail with an approximately 50:50 energy distribution between the pulse and tail. The energy per pulse was 1.3 J.

(7) A 15-cm focal length NaCl lens was used to focus the beam. During a photolysis, the focal point was located at approximately the midpoint of the cell. The laser beam was attenuated by placing a gas cell containing SF₆ in front of the photolysis cell. The intensity was varied by changing the pressure of SF₆. The energy density at the focal point was 46 J/cm^2 at 0.8 J/pulse and 23 J/cm^2 at 0.4 J/pulse.

(8) At low fluencies, **7** was not observed, presumably due to lack of secondary decomposition of **6**.
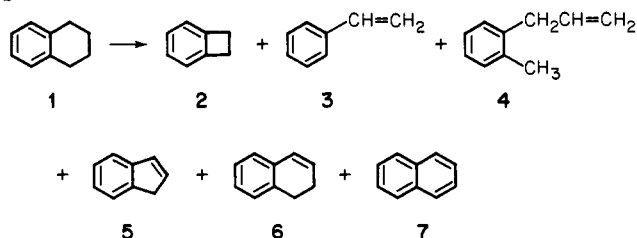
(9) Phenylacetylene was identified by GC (MS)–mass spectroscopy of the photolysis mixture. It was not a product in the flow pyrolysis or the sensitized photolysis. In the direct irradiation experiments, this product could result from dehydrogenation of vibrationally excited styrene.

Table I. Product Distribution for Thermal Reaction of 1

| | products, % | | | | | | | % conversion |
conditions	2	3	4	5	6	7	other	of 1
flow pyrolysis, 1 atm of N_2, quartz reactor, 750 °C	2.4[a,b]	18.3	0.5	17.5	10.7	45.8	4.2	74.8
vacuum flash pyrolysis, 0.05 torr, quartz reactor, 750 °C	34.7	9.9	7.9	4.1	31.8	8.2	3.4	3.7
multiphoton excitation, 0.325 torr 1, energy/pulse 0.4 J, 13 020 pulses	72.6	11.7[c]	3.4	4.2	6.2	0.0	2.0	0.5
multiphoton excitation,[d] 0.325 torr 1, energy/pulse 0.8 J, 2790 pulses	54.8	19.7[c]	2.6	5.5	9.0	trace	8.4	0.8
SiF_4 sensitization,[11] T_{max} 650 °C, 5 torr SiF_4, 0.325 torr 1, 4960 pulses	58.5	8.3	20.8	2.2	10.3	0.0	0.0	1.5
SiF_4 sensitization,[11] T_{max} 1490 °C, 6 torr SiF_4, 0.325 torr 1, 180 pulses	38.2	20.1	8.4	9.4	15.5	5.6	2.8	7.7

[a] Numbers are percent of total product found. [b] All data have been corrected for FID response. [c] Includes phenylacetylene response. [d] Visible emission in the focal region was observed in this experiment.

Scheme I

Table II. Deuterium Labeling in Products from Photolysis of 1-d_4[a]

| | % of total mixture | isotopomer, % | | | |
product		d_4	d_3	d_2	d_1
2	57.8	100[b,c]	0	0	0
3	10.6	32	8	29	31
4	8.2	100	0	0	0
5	4.2	0	42	43	15
6	12.8	10	83	7	0
7	2.3	0	1	95	4

[a] Photolysis conditions: 1-d_4 (0.325 torr) was irradiated with 300 pulses, 0.27 J/pulse, with 5 torr SiF_4. T_{max} was 1240 °C. [b] The numbers are the percent of product with the indicated number of deuterium atoms as determined by GC-MS analysis.[16] [c] The data are corrected for ^{13}C natural abundance and 98.7% deuterium incorporation in 1-d_4.

were irradiated[11] with an unfocused, pulsed CO_2 TEA laser tuned to 1027.36 cm^{-1}. Pure tetralin does not decompose under unfocused conditions; thus, all chemistry is due to sensitization by SiF_4. All six major products were again found.

The number of pulses and the maximum temperature[12] of SiF_4 both had pronounced effects on the product distribution. The variation in the number of pulses had a number of effects. With an increasing number of pulses, the percentage of 2 and 6 decreased and the percentage of 3, 5, and 7 increased. This is consistent with 2 and 6 being primary products and at least some fraction of 3, 5, and 7 being derived from them. Sensitized photolysis[13] of 2 gave rise to a clean isomerization to 3, the sole product of the reaction (70% conversion). Sensitized photolysis[13] of 6 (20% conversion) gave rise to two major products,[14] 7 (68% of product) and 5 (11%).

Temperature variation was achieved by changing the beam intensity and by varying the sensitizer pressure. Less secondary decomposition took place at lower temperatures, and there was a partitioning between the retro-[2 + 4] channel and the dehydrogenation channel (see Table I). The ethylene-loss channel increased relative to dehydrogenation as the temperature was lowered, consistent with it being the low-energy reaction channel for tetralin.

In order to further elucidate the mechanism of reaction of tetralin, 1,1,4,4-tetradeuteriotetralin (1-d_4) was synthesized[15] and subjected to sensitized photolysis. The labeling results[16] indicate that the retro-[2 + 4] product results entirely from C_2H_4 loss and

the dehydrogenation *is predominantly a result of 1,2-elimination* (see Table II). They also suggest that there is at least one pathway leading to 3 which bypasses 2.

Since thermal 1,2-elimination of hydrogen is unusual,[17] the nature of this reaction is of interest. The surface to volume ratio[18] for the photolysis cell had no effect on the ratio of ethylene loss to dehydrogenation for the sensitized photolysis. The possibility of a radical chain mechanism for the dehydrogenation was tested for by charging the photolysis cell with 1 torr of nitric oxide. The only observed effect of nitric oxide was to lower the effective temperature for the photolysis.[19] A decrease in the partial pressure of tetralin from 0.325 to 0.032 torr also had no effect on the ratio of ethylene loss to dehydrogenation.

We draw the following conclusions from the above experiments: (1) Some fraction of the dehydrogenation reaction in the flow reactor is surface catalyzed. This leads to an anomalously large amount of 1,2-dihydronaphthalene and naphthalene in the reaction products in these flow-pyrolysis studies and very likely in all previous investigations. (2) The lowest energy homogeneous reaction channel for tetralin is the retro-[2 + 4] channel, giving rise to benzocyclobutene. This fact is borne out in both the multiphoton- and SiF_4-sensitized experiments, where surface chemistry does not appear to be important. (3) The low-energy dehydrogenation channel of tetralin is almost exclusively 1,2-dehydrogenation. This process, if concerted, is symmetry forbidden and without precedent as the lowest energy dehydrogenation channel in cyclic olefins. Evidence for a radical pathway by radical-scavenging experiments was not found. Bimolecular

(10) K. J. Olzyna, E. Grunwald, P. M. Keehn, and S. P. Anderson, *Tetrahedron Lett.*, 1609 (1977).

(11) The photolysis cell for the sensitized photolysis was 4.5-cm i.d. by 4-cm long. The energy/pulse ranged from 0.11 to 0.27 J/pulse, and the beam diameter was 0.7 cm. The energy absorbed ranged from 0.024 to 0.14 J/pulse. The variation in beam intensity was achieved as described in ref 7.

(12) The initial temperature after a pulse was calculated by assuming all absorbed energy is statistically distributed among all of the degrees of freedom of SiF_4 and 1.

(13) Photolysis conditions:[11] 300 shots, 0.27 J/pulse, 5 torr SiF_4, and 0.325 torr 2 or 6.

(14) Minor products were 1,4-dihydronapthalene (7% of product), 1 (5%), 3 (3%), and six unidentified products (total 5.9%).

(15) Tetralin labeled with deuterium in the benzylic positions was obtained by treating 1 with dimsyl-d_5 anion in dimethyl-d_6 sulfoxide.

(16) Analyses for isotope distribution in each of the pyrolysis products of 1-d_4 were obtained by GC-MS. The mass spectral data were obtained at 15 eV.

(17) D. C. Tardy, R. Ireton, and A. S. Gordon, *J. Am. Chem. Soc.*, 101, 1508 (1979).

(18) The surface to volume ratio was increased by a factor of four by using a cell 4.5 cm i.d. by 1 cm long.

(19) We are not confident that NO is an irreversible radical scavenger at these temperatures. However, we are concerned that other potential scavengers would undergo decomposition more efficiently than tetralin under our reaction conditions.

pathways for this process were also not detectable by changing the partial pressure of **1**.

The reactivity of tetralin contrasts with that of its olefinic analogue, cyclohexene,[17] in a number of ways. The rate of the retro-[2 + 4] reaction is more nearly comparable to that of dehydrogenation in tetralin, resulting in competitive formation of **6** and **7** with **2** and **3**. If the retro-[2 + 4] reaction in tetralin is concerted, disruption of the aromatic nature of the ring system may give rise to a higher energy transition state for ethylene loss. If the concerted pathway is shunned due to this situation, a stepwise carbon–carbon bond cleavage with subsequent loss of ethylene may be occurring. In either case, one would expect a higher activation energy for the ethylene-loss channel, one more nearly comparable to that of dehydrogenation. The observation of o-allyltoluene, the disproportionation product from the intermediate in a stepwise process, indicates that the nonconcerted reaction is energetically feasible. The occurrence of 1,2- instead of 1,4-dehydrogenation is perhaps not surprising since again the aromatic nature of the ring system must be destroyed for a concerted 1,4-hydrogen elimination to occur. Questions as to the energetics of these processes and their mechanisms are under active investigation.

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Received March 5, 1980

Synthesis of Metallacyclopentanes Containing Two Metals in the Ring. Thermal Decomposition to Cyclopropane and Ligand-Induced Conversion to Stable Mononuclear Metallacyclopentanones
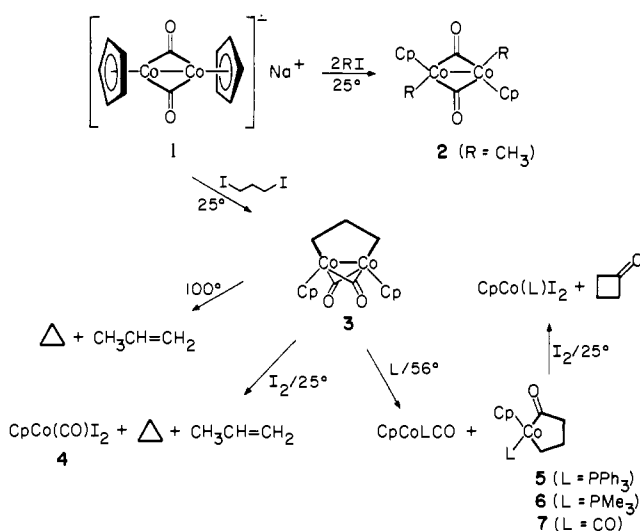
Sir:

During the past few years, much successful effort has been directed toward the synthesis of metallacycles and the study of their chemical reactions. This research has revealed similarities and differences between metallacycles and their noncyclic counterparts that has increased our understanding of the chemical behavior of both types of complexes; it has also allowed identification of metallacyclic intermediates in a number of important catalytic processes.[1]

It is our view that metallacycles containing two, rather than just one, metal atoms will provide similar illumination of the chemistry of binuclear dialkyl complexes. We now report the successful synthesis of a five-membered ring metallacycle containing two cobalt atoms and a study of the reactions of this material.[2]

Scheme I

Scheme I

Our synthesis is based on an intramolecular version of the earlier-reported[3] dialkylation of sodium di-μ-carbonyl-bis(η^5-cyclopentadienyl)cobaltate (**1**) to give **2** and other alkyls (Scheme I). Addition of 1.5 equiv of 1,3-diiodopropane to a stirred suspension of green radical anion **1** in THF caused the color of the solution to change immediately, first to an intense blue-green and then to greenish brown. At the same time, the characteristic absorptions of **1** were replaced by a transient absorption at 1790 cm^{-1} [assigned[4] to the neutral dimer $Cp_2Co_2(CO)_2$] and a band at 1815 cm^{-1}. Column chromatography (aluminum oxide, air-free conditions) of the material so obtained afforded μ-trimethylene-di-μ-carbonyl-bis(η^5-cyclopentadienyl)dicobalt (**3**) in 40% yield.[5,6]

Our preliminary results on the chemistry of bimetallacycle **3**, as well as on some of its reaction products, are summarized in Scheme I. Thermally, the material is surprisingly stable. Whereas the dimethyl derivative **2** undergoes solution thermal decomposition rapidly at temperatures near ambient, in benzene **3** decomposes only slowly at 100 °C (sealed tube). The product of this decomposition is primarily propene (73%), but substantial amounts of cyclopropane (17%), as well as traces of propane (1.4%), are produced (values given are absolute yields determined by gas chromatography, using an internal standard). Crossover experiments demonstrated the process is intramolecular: a 50:50 mixture of **3**-d_0 and **3**-d_4 (labeled in the α-CH_2 positions) gives only cyclopropane-d_0 and -d_4, uncontaminated with significant

(1) See, for example: (a) Y. Wakatsuki, K. Aoki, and H. Yamazaki, *J. Am. Chem. Soc.*, **101**, 1123 (1979); (b) D. R. McAlister, J. E. Bercaw, and R. G. Bergman, *ibid.*, **99**, 1666 (1977); (c) M. Sohn, J. Blum, and J. Halpern, *ibid.*, **101**, 2694 (1979); (d) J. X. McDermott, J. F. White, and G. M. Whitesides, *ibid.*, **95**, 4451 (1973), and references cited therein; (e) R. H. Grubbs, A. Miyashita, M. Liu, and P. Burk, *ibid.*, **100**, 2418 (1978), and references cited therein; (f) S. J. McLain, C. D. Wood, and R. R. Schrock, *ibid.*, **101**, 4558 (1979); (g) R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *ibid.*, **101**, 364 (1979), and references cited therein; (h) K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green, and R. Mahtab, *J. Chem. Soc., Chem. Commun.*, 604 (1978).

(2) A few binuclear metallacycles are known or have been postulated as intermediates in certain organometallic transformations; see, for example: (a) S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 221 (1978); (b) D. J. S. Guthrie, I. U. Khand, G. R. Knox, J. Kollmeier, P. L. Pauson, and W. E. Watts, *J. Organomet. Chem.*, **90**, 93 (1975); (c) F. Garnier, P. Krausz, and J.-E. Dubois, *ibid.*, **170**, 195 (1979); (d) P. Pertici and G. Vitulli, *Tetrahedron Lett.*, 1897 (1979); (e) C. E. Sumner, Jr., P. E. Riley, R. E. Davis, and R. Pettit, *J. Am. Chem. Soc.*, **102**, 1752 (1980).

(3) (a) N. E. Schore, C. S. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, **98**, 7436 (1976); (b) M. A. White and R. G. Bergman, *J. Chem. Soc., Chem. Commun.*, 1056 (1979); (c) R. G. Bergman, *Acc. Chem. Res.*, **13**, 113 (1980).

(4) (a) N. E. Schore, C. S. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 1781 (1977); (b) W. I. Bailey, Jr., D. M. Collins, F. A. Cotton, J. C. Baldwin, and W. C. Kaska, *J. Organomet. Chem.*, **165**, 373 (1979).

(5) Data for **3**: mp 170 °C (dec); IR (THF) 1850 (w), 1815 (s), 1785 (w) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 4.71 (s, 10), 1.66 (t, 4), 0.68 (q, 2); ^{13}C NMR (benzene-d_6) δ 254.8, 91.75, 31.9, 20.5; mass spectrum (MS) (15 eV), m/e 346 (M$^+$). Anal. Calcd for $C_{15}H_{16}Co_2O_2$: C, 52.05; H, 4.66. Found: C, 52.33; H, 4.91.

(6) In preliminary results, we have also found that radical anion **1** reacts with methylene iodide to give the μ-methylene complex analogous to **3**. This material is isolated as dark red crystals in 48% yield: mp 68 °C; IR (THF) 1996, 1957, 1924 cm^{-1}; MS (15 eV), m/e 318 (M$^+$); high-resolution mass spectroscopy (HRMS) calcd for $C_{13}H_{12}Co_2O_2$, 317.9501; found, 317.9492. Substituted analogues of this complex have been prepared earlier; see, for example: (a) W. A. Herrmann, *Chem. Ber.*, **1**, 1077 (1978); (b) W. Herrmann and I. Schweizer, *Z. Naturforsch. B: Anorg. Chem., Org. Chem.*, **33B**, 911 (1978).