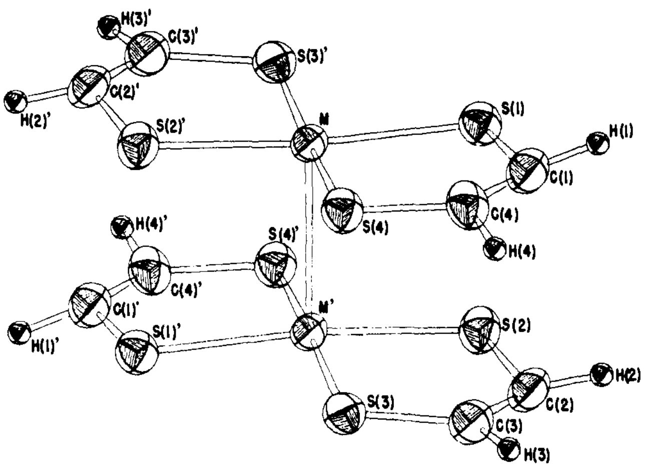

Figure 1. Molecular structure of $(MS_4C_4H_4)_2$, M = Pd, Pt.

attention in the recent past.[1] A large number of 1,2-dithiolene complex crystal structures have been reported. Most of these contain monomeric units with the central metal atom surrounded by four sulfur atoms in a near-perfect square-planar arrangement. Also, structures containing dimeric units with the metal surrounded by five sulfur atoms have been described for complexes of some of the lighter transition metals.[2] We report here the first examples of dimeric 1,2-dithiolene complexes with direct metal–metal bonding. The unique structure of these complexes has important implications to both the understanding of bisdithiolene structures and to metal–metal bonding in coordination compounds.[3]

The complexes studied are derivatives of the ethylene 1,2-dithiolate ligand and have the empirical formula $MS_4C_4H_4$ (M = Ni, Pd, Pt). They were prepared by iodine oxidation of the salts $(Pr_4N^+)(Ms_4C_4H_4^-)$, using the method of Hoyer, *et al.*[4] The synthesis and some properties of $NiS_4C_4H_4$ have been discussed previously,[5] but $PdS_4C_4H_4$ and $PtS_4C_4H_4$ are reported here for the first time.

Marked differences in the electrical conductivity and X-ray powder diffraction patterns, of $NiS_4C_4H_4$ on the one hand, and $PdS_4C_4H_4$ and $PtS_4C_4H_4$ on the other,[6] led us to single-crystal X-ray diffraction studies on each of the three neutral complexes. Single crystals of each compound were grown from CS_2 solution by slow cooling or evaporation. Complete three-dimensional single-crystal X-ray diffraction data were taken with Cu Kα radiation using a GE490 automated diffractometer. The structures were solved by means of Patterson and Fourier syntheses and refined by least squares.

The details of the structure of $NiS_4C_4H_4$ are in agreement with the preliminary data of Höhne, *et al.*,[7] and the complete structural investigation of Smith.[8] This compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.90$, $b = 6.00$, $c = 6.47$ Å, $\beta = 93.9°$, $Z = 2$; the units are monomeric and have no exceptionally close intermolecular contact.

$PtS_4C_4H_4$ and $PdS_4C_4H_4$ are isostructural and crystallize in the monoclinic space group $P2_1/n$. Crystal data for $PdS_4C_4H_4$ are $a = 9.916$, $b = 11.788$, $c = 6.472$ Å, $\beta = 92.21°$, $Z = 4$; for $PtS_4C_4H_4$ $a = 9.97$, $b = 11.87$, $c = 6.47$ Å, $\beta = 92.0°$, $Z = 4$. At the present stage of refinement, $R = 0.064$ (F basis) for $PdS_4C_4H_4$ (1349 independent reflections) and $R = 0.092$ for $PtS_4C_4H_4$ (1116 independent reflections). The molecular structure of the $MS_4C_4H_4$ (M = Pd, Pt) complexes, shown in Figure 1, consists of two essentially planar $MS_4C_4H_4$ units joined by a direct metal–metal bond. In the Pd structure, each metal atom is drawn inward from the plane of four S atoms by 0.12 Å to give a Pd–Pd distance of 2.79 Å; the corresponding Pt–Pt distance is 2.77 Å. These distances are comparable to those observed in the metal and are among the shortest ever observed in coordination complexes of Pd and Pt.[9] The eight sulfur atoms of the dimer form a slightly distorted cube with the S–S distances between $MS_4C_4H_4$ units (average 3.026 Å) slightly shorter than those within the $MS_4C_4H_4$ units (average 3.253 Å).

This novel molecular arrangement is quite distinct from the laterally displaced dimeric structures exhibited by several other bisdithiolene complexes, where interactions between the dimer halves are of the metal–sulfur type.[2] Certain features of this structure, such as the approximately square arrangement of sulfur atoms at the faces of the S_8 polyhedra and the relatively short S–S distances, bear resemblance to the trigonal-prismatic geometry found for several of the tris-1,2-dithiolene complexes, where S–S bonding is believed to be important in stabilizing the molecular structure.[10]

Preliminary molecular weight and mass spectral data for $PtS_4C_4H_4$ indicate a monomeric structure for this complex both in solution and in the vapor state. The detailed results of these studies and complete structural information will be reported subsequently.

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Physical Parameters and Crystal Structure of a Unique Pentacoordinate Copper(II) Hippurate Dimer

Sir:

Authentic five-coordinate complexes of the first-row transition metals are being reported with increasing frequency.[1-3] In general, they are formed with simple monoatomic or diatomic ligands such as halide or carbonyl, or they are formed by polydentate ligands which

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tend to force a particular geometry. Both types of coordination compounds are known for copper(II). The simple five-coordinate type is represented by $CuCl_5^{3-}$, which has been shown to have a trigonal-bipyramidal structure.[4] The more complex species are represented by [Cu(*N*,*N'*-di(3-aminopropyl)piperazine)-Cl][ClO_4], which has been found to have a square-pyramidal geometry with N atoms in the base and the chloride in the apical position.[5] In addition, copper(II) forms five-coordinate species with a variety of amino acids and peptide model compounds.[6] In these complexes, the geometry about the copper atom is approximately square pyramidal, with amino or peptide nitrogens and carboxyl or peptide oxygens in the base and either a water molecule or a carboxyl oxygen (from a neighboring ligand) in the apical position. No examples of oxygen-bridged dimers or monodentate organic ligands have been reported. This communication reports the preparation and characterization of a five-coordinate Cu(II) dimer of the hippurate anion.

A compound of empirical formula $Cu[(C_6H_5)CONHCH_2COO]_2 \cdot 4H_2O$ was prepared by mixing sodium hippurate and $Cu(ClO_4)_2 \cdot 6H_2O$ in a 3:1 molar ratio in a 30% methanol-in-water solvent at 50°. Light blue crystals were filtered from the cooled solution after standing for approximately 12 hr. The crystals melted with decomposition at 239–241°. An intermediate blue-green color was observed at 90–95°. The compound was recrystallized from the methanol–water mixture in an attempt to obtain more suitable crystals for the X-ray crystallographic study.

The compound crystallizes in the monoclinic space group $P2_1/c$ with four formula weights in a unit cell of dimensions $a = 7.25$, $b = 40.16$, $c = 7.46 \pm 0.01$ Å, and $\beta = 102.6 \pm 0.10°$. A preliminary set of diffractometer data was taken on a crystal of admittedly poor quality, out to a 2θ limit of 70° using Cu Kα radiation. In the subsequent refinement, 763 independent and statistically significant structure factors were used. At the present stage of isotopic refinement, the structure has a value of $R = 0.078$.

The structure revealed by this study has a number of unique features: the hippurate ions are monodentate, bonding only through the carboxyl oxygen; the compound exists as a bridged dimer with the bridging occurring through a single carboxyl oxygen; and finally, each copper ion is five-coordinate, having a distorted [4 + 1] tetragonal-pyramidal geometry. Each monomeric unit contains a tetragonally arranged copper ion bonded trans to the oxygen of two water molecules (2.00 ± 0.02 Å) and to the carboxyl oxygens of two hippurate groups (1.92 ± 0.02 Å). Angles within this plane approximate 90°, varying from 88 to 91°. Molecular parameters within the hippurate ligands closely approximate those found in a recently published study[7] on hippuric acid itself. The copper dimer consists of two of these monomeric units bridged through carboxyl oxygens of two hippurates. One of these hippurates sits at an angle of 78° to the tetragonal plane and forms the apical ligand to the copper. Thus, each copper ion is bonded to two bridged hippurates (2.32, 1.93 Å), one uniquely attached hippurate (1.93 Å), and two water molecules, resulting in five-coordinate, distorted square-pyramidal geometry. The Cu–Cu separation of 3.30 Å is long enough to preclude any Cu–Cu bonding.[6] Figure 1 shows a projectional view of the dimer.

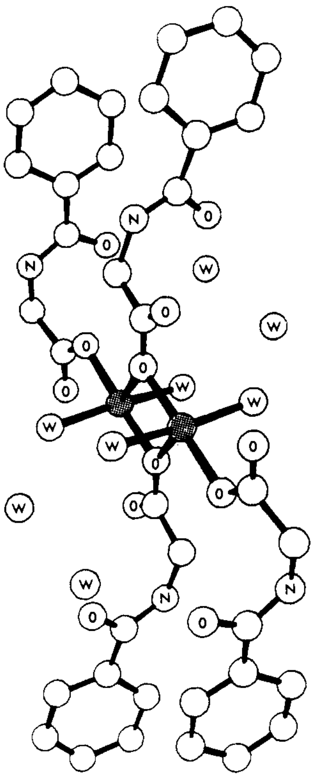

Figure 1. Projectional view of Cu(II) hippurate dimer (W, water oxygen; N, amide nitrogen; O, oxygen).

A comparison of the structure reported here with those of some of the copper(II) complexes of amino acids and peptide molecules indicates some very interesting differences. First, the amide nitrogen is not bonding, although, if it were, it would provide a five-membered chelate ring with the bonding carboxyl oxygen. Thus, under the preparative conditions used here, the amide nitrogen is not deprotonated, and therefore does not react with the metal. Similar results are reported for the interaction of copper(II) with glycylglycylglycine, provided the pH is maintained below 5.[8] The values of the Cu–ligand distances in the square base are comparable to the average values reported by Freeman:[6] Cu–O (carboxyl in nonchelate ring), 1.97 Å; Cu–OH_2, 1.97 Å. The Cu–O (bridging carboxyl) distance in the apical position is very nearly equal to the limiting value of 2.3 Å calculated by considering the Jahn–Teller distortion.[6]

The magnetic moment for the dimer was determined by the Gouy method to be approximately 1.9 BM per copper ion at room temperature, indicating normal paramagnetic behavior. There appears to be no spin delocalization through the bridging oxygens, although the Cu–O distances are minimal. The diffuse reflectance spectrum for the solid dimer has λ_{max} $\sim$680 nm, with a pronounced shoulder at $\sim$880 nm. This spectrum is consistent with a distorted square-pyramidal

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field[2] and a coordination sphere of five bonded oxygen atoms.[6] Work is in progress to ascertain the relationship of the solid species reported here to the species formed in solution. In addition, the effect of dehydration on the structure is being determined, and efforts are being made to prepare a comparable compound from basic media.

Acknowledgment. The authors wish to express their gratitude to the National Science Foundation (No. GU-2632) and E. R. Squibb and Sons, Inc., for financial assistance to support this and subsequent studies.

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[9] (a) Address requests for reprints and for information on the preparation and properties of the compound to this author; (b) address requests for information on the X-ray structure determination to this author.

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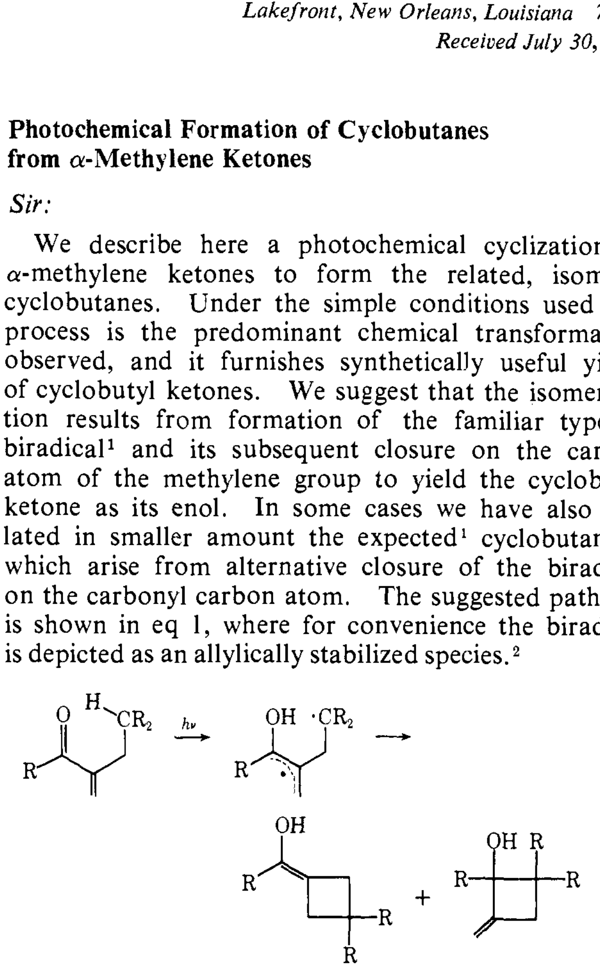
Photochemical Formation of Cyclobutanes from α-Methylene Ketones

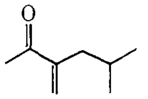
Sir:

We describe here a photochemical cyclization of α-methylene ketones to form the related, isomeric cyclobutanes. Under the simple conditions used this process is the predominant chemical transformation observed, and it furnishes synthetically useful yields of cyclobutyl ketones. We suggest that the isomerization results from formation of the familiar type II biradical[1] and its subsequent closure on the carbon atom of the methylene group to yield the cyclobutyl ketone as its enol. In some cases we have also isolated in smaller amount the expected[1] cyclobutanols, which arise from alternative closure of the biradical on the carbonyl carbon atom. The suggested pathway is shown in eq 1, where for convenience the biradical is depicted as an allylically stabilized species.[2]



(1)

The α-methylene ketones employed are compounds **1**–**4**. Of these, **1**[3] and **2**[3] were prepared by acid-catalyzed Mannich reaction[4] of formaldehyde, diethylamine hydrochloride, and the appropriate saturated ketone, followed by thermal β elimination from the Mannich base. The cyclohexyl-substituted ketone **3** was synthesized from known[5] ethyl 2-cyclohexylacetoacetate (**5**). This keto ester was converted to its ethylene ketal (**6**) and then reduced with lithium aluminum hydride; the alcohol **7** thus formed was treated directly with acid to furnish **3**[3] in an overall yield of 78%. The cycloheptyl homolog **4**[3] was available (88%) by a similar sequence from ethyl 2-cycloheptylacetoacetate,[3] itself prepared by alkylation of the potassium salt of acetoacetic ester with cycloheptyl iodide[6] in diglyme. Each of these ketones (**1–4**) was purified by preparative vpc,[7] and characterized by ir and nmr spectroscopy.



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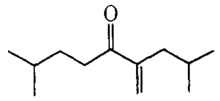

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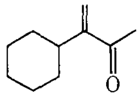

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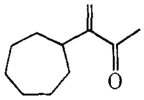

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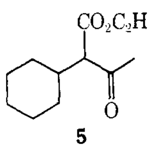

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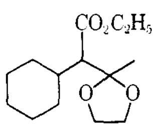

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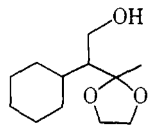

7

Irradiation[8] of **1** in pentane for 64 hr caused destruction of 89% of the starting material and formation of two products. The major of these (68%[9]) was 3,3-dimethylcyclobutyl methyl ketone (**8a**),[3] identical with a sample prepared by reaction[10] of 3,3-dimethylcyclobutanecarboxylic acid (**8c**)[11] with methyllithium in ether. The minor photochemical product (19%[9]) was recognized as the type II cyclobutanol **9a**[3] [oil; ir 3620 (m), 3475 (w), 3070 (w), 2960 (s), 2865 (m), 1680 (w),[12] 880 cm^{-1}; nmr δ 1.02 (s) and 1.07 (s) (6 H), 1.22 (s, 3 H), 1.55 (s, 1 H, exchanges with D_2O), 2.12 (m, 2 H), 4.77 (m, 1 H), 5.02 (m, 1 H)].

A parallel reaction occurred on photolysis of **2** (40 hr, 100% conversion). In this case the major product, cyclobutyl ketone **8b**[3] (67%[9]), was independently prepared by reaction[13] of diisoamylcadmium with the acyl chloride from **8c**. The minor product (12%[9]) was cyclobutanol **9b**[3] [oil; ir 3620 (m), 3480 (w), 3070 (w), 2960 (s), 2875 (s), 1680 (w),[12] 1470 (m), 880 cm^{-1}; nmr δ 0.92 (d, J = 5 Hz), 1.05 (s), and 1.08 (s) (12 H), 1.4 (m, 6 H), 2.1 (m, 2 H), 4.80 (m, 1 H), 4.95 (m, 1 H)]. This isomerization of **2** to **8b** and **9b** is readily under-

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[2] Similar closure of type II biradicals from two cyclopentenones is described by W. C. Agosta and A. B. Smith, III, *J. Amer. Chem. Soc.*, **93**, 5513 (1971).

[3] This new compound gave satisfactory elemental analysis for carbon and hydrogen after purification by preparative vpc.

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[7] Vapor phase chromatography (vpc) was carried out under conditions similar to those described in ref 2.

[8] Irradiations were carried out on dilute (1 mg/ml) solutions with a Hanovia Model L mercury lamp (No. 679A-36) in a quartz immersion well using a Corning No. 3320 uranium glass filter (λ >3300 Å). Benzene was solvent unless otherwise indicated.

[9] Reported yields were obtained by calibrated vpc measurements and are based on converted starting material.

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[12] The methylene stretching frequency is known to be a sensitive function of environment; this value is typical of methylenecyclobutanes: L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, Chapter 3; "Advances in Infrared Group Frequencies," Methuen, London, 1968, Chapter 2.

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