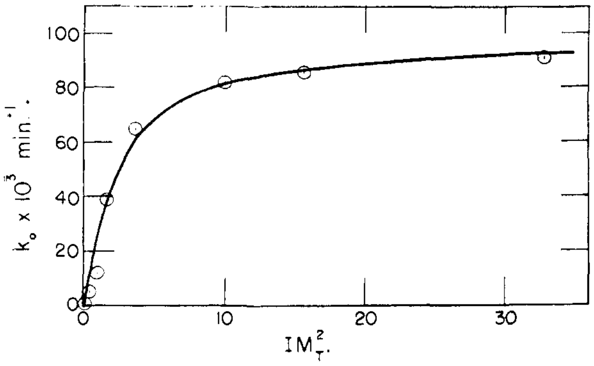


Fig. 3.—Plot of the observed first order rate constants (k_0) for the appearance of I_2 *vs.* the square of the concentration of total imidazole. The points are experimental and the curve is that obtained from equation 3.

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} D \qquad (2)$$

where C is at low steady state. With increasing imidazole concentration $k_0$0 proceeded from second order to zero order dependence in imidazole concentration (Fig. 3). Thus, Michaelis–Menten type kinetics are followed (3)

$$k_0 = \frac{0.95 \times 10^{-2}(IM_T)^2}{0.20 + (IM_T)^2} \qquad (3)$$

where k_0 is the observed rate of attainment of equilibrium and IM_T the total concentration of imidazole (*i.e.*, $IM_T = IM + IM^+H$). The results enumerated above suggest two alternative explanations for the imidazole catalysis: (a) saturation of I_1 by two molecules of an imidazole species followed by an intracomplex general base and/or general acid catalysis of the prototropic shift leading to I_2; and/or (b) the catalysis of the formation of I_1 involving two molecules of an imidazole species is rate determining at low IM_T concentration but at high IM_T concentration the non-catalyzed prototropic shift of I_1 to I_2 becomes rate determining and the reaction changes from second to zero order in IM_T. Replacement of pyridoxal by its morpholine imine does not unduly affect the over-all rate, suggesting that the rate-determining step is in fact the prototropic shift. Furthermore, the kinetic treatment is based upon the assumption of a rate-determining prototropic shift and has been found to predict accurately the effect of variation of the initial reactant concentrations upon the observed overall rates.

Following the attainment of equilibrium in I_2 the second and slower phase of the reaction is encountered in which equilibrium is attained between all species [*i.e.*, amino acid + pyCHO $\rightarrow I_1 \rightleftarrows I_2 \rightleftarrows$ pyNH$_2$ + keto acid]. The second phase is accompanied by an increase in absorbance at the isosbestic points for the first phase, appearance of new isosbestic points at 310, 350 and 260 mμ, decreased absorbance at 395 mμ (continuing decrease in pyCHO concentration) and decreased absorbance at 246 mμ (the absorbance by I_2 + pyCHO + amino acid at 246 mμ is greater than that of pyNH$_2$ + keto acid produced). The pH-dependence of the imidazole-catalyzed reaction, details of the kinetics and equilibrium constants and a discussion of the possible mechanism for catalysis will be submitted for publication shortly.

The present results open the door to the possible establishment in aqueous solution of similar model systems of the racemization, decarboxylation and C_α—C_β bond scissions of α-amino acids which are mediated by enzymes requiring pyridoxal phosphate as cofactor. Investigation of these possibilities is being actively pursued.

[8] This work was supported by grants from the National Institutes of Health and the National Science Foundation.

[9] Post-doctoral Fellow, Department of Chemistry, Cornell University.

DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, N. Y.
THOMAS C. BRUICE[8]
RICHARD M. TOPPING[9]

RECEIVED APRIL 21, 1962

THE MOLECULAR STRUCTURE OF $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$

Sir:

The reactions of acetylenes with metal carbonyls or other transition metal compounds have yielded a wide variety of organometallic complexes. Compounds of two general types have been prepared in which the acetylenes either (1) form new carbon–carbon bonds by polymerization or reaction with other ligands present or (2) complex to a metal without formation of new carbon–carbon bonds. The former group[1-5] includes compounds with metals bonded to organic ring systems (with or without incorporated CO groups); the ring system may be heterocyclic with a transition metal as the hetero atom.[5] To date the only known structures of the latter group of compounds,[6] in which acetylene remains as a distinct recognizable entity, have involved acetylenes which form metal complexes either via one[7] or two[8,9] μ-type bonds[10] or via two "bent" σ-bonds.[1,2a,11]

[1] G. E. Coates, "Organometallic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960.

[2] (a) G. E. Coates and F. Glocking, "Organometallic Chemistry," edited by H. Zeiss, Reinhold Publishing Corp., New York, N. Y., 1960, pp. 458–463; (b) J. Chatt, P. L. Pauson and L. M. Venanzi, *ibid.*, pp. 492–498; (c) H. Zeiss, *ibid.*, pp. 411–417.

[3] D. W. A. Sharp, "Annual Reports on the Progress of Chemistry," The Chemical Society (London), **56**, pp. 140–143 (1959); **57**, pp. 147–148 (1960).

[4] P. L. Pauson, *Proc. Chem. Soc.*, 297 (1960).

[5] (a) W. Hübel, E. H. Braye, A. Clauss, E. Weiss, U. Krüerke, D. A. Brown, G. D. S. King and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959); (b) W. Hübel and E. H. Braye, *ibid.*, **10**, 250 (1959); (c) E. H. Braye, C. Hoogzand, W. Hübel, U. Krüerke, R. Merényie and E. Weiss, "Advances in the Chemistry of the Coordination Compounds," edited by S. Kirschner, The Macmillan Co., New York, N. Y., 1961, pp. 190–198; (d) G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5307 (1959).

[6] Transition metal acetylides or metal acetylene complexes with the acetylene possessing additional coördinating groups capable of interacting with a metal atom (*e.g.*, hydroxyacetylenes) are not included in this classification.

[7] F. L. Carter and E. W. Hughes, *Acta Cryst.*, **10**, 801 (1957); S. V. Bukhovets and N. K. Pukhova, *Zhur. Neorg. Khim.*, **3**, 1714 (1958); J. Chatt, L. A. Duncanson and R. G. Guy, *Chem. and Ind.*, 430 (1959); J. Chatt, R. G. Guy and L. A. Duncanson, *J. Chem. Soc.*, 827 (1961).

[8] H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby and I. Wender, *J. Am. Chem. Soc.*, **78**, 120 (1956); W. G. Sly, *ibid.*, **81**, 18 (1959).

[9] J. F. Tilney-Bassett and O. S. Mills, *J. Am. Chem. Soc.*, **81**, 1757 (1959); M. Dubeck, *ibid.*, **82**, 502 (1960); J. F. Tilney-Bassett, *J. Chem. Soc.*, 577 (1961).

We wish to report the results of an X-ray study of $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$ which has revealed the first known case of a molecular metal–acetylene complex in which the acetylene donates 4-electrons via two σ-bonds and a "bent" μ-type bond.[10] This compound prepared by Krüerke and Hübel[12] was generously made available by Dr. Hübel.

The black crystals of symmetry C2/c contain eight molecules in a unit cell of dimensions a = 15.44 Å., b = 9.65 Å., c = 27.42 Å., and β = 92°-05′. A three-dimensional structural analysis including isotropic least squares refinement[13] and error analysis[14] has yielded the molecular configuration (Fig. 1). The reliability index, R_1, is 7.2% for 1660 observed reflections.

The structure consists of discrete $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$ molecules in which the acetylene fragment functions as an olefinic coördinating group by forming σ-bonds with two cobalts, Co_2 and Co_3, and a "bent" four-centered[15] μ-type bond with the other two cobalts, Co_1 and Co_4. The cobalts are also interconnected by metal–metal bonds and two unsymmetrical bridging carbonyl groups. The configuration of the cobalt atoms can be achieved by a symmetrical distortion of a tetrahedron of cobalt atoms (as found in $Co_4(CO)_{12}$[17]) to give a "butterfly" form with a dihedral angle of 118°. The approximate C_{2v} point symmetry of the cobalt atoms relates Co_1 with Co_4 and Co_2 with Co_3 and results in three different Co-Co distances. The non-bonding $Co_1 \ldots Co_4$ distance is 3.55 Å.; the bonding Co_2–Co_3 distance of 2.55 Å. is approximately 0.1 Å. longer than the average distance of 2.43 Å. for the other four equivalent Co–Co bonds. The idealized configuration for the $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$ molecule retains only the cobalts' twofold axis; no special molecular symmetry is required by the space group, since all atoms are in general positions.

As expected from the compound's diamagnetism, the electronic configurations of both types of cobalts conform to the "inert gas rule." Each of the seven coördinated Co_2 and Co_3 atoms forms σ-bonds with the three other cobalts, two terminal carbonyls, one bridging carbonyl, and one carbon of the olefinic group. Each of the other two cobalts, Co_1 and Co_4, is linked to six coördinating groups—Co_2 and Co_3, two terminal carbonyls, one bridging carbonyl, and the olefinic moiety. Although the olefinic carbons are not equidistant from either Co_1 or Co_4 (*i.e.*, an average difference of 0.13 Å. is found), a two π-electron donation to both cobalts by a delocalized μ-type bond is required for a "closed" shell electronic ground state. A net charge transfer from the olefinic double bond to the two cobalts is indicated by the lengthening of the C_{13}–C_{14} bond to 1.44 Å.; similarly increased bond lengths are observed for other simple metal–olefin complexes.[18] This double bond interaction with two metals, found in $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$, is the first known example of its kind; a formally analogous diene interaction with two metals involving four π-electrons is known for one isomer of $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$.[19] A qualitative MO description of these types of bonding has been formulated by Brown.[20] The nature of bonding of the acetylene group in $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$ resembles somewhat the bonding found in thorium dicarbide in which each C_2 group interacts with six thorium atoms.[21]

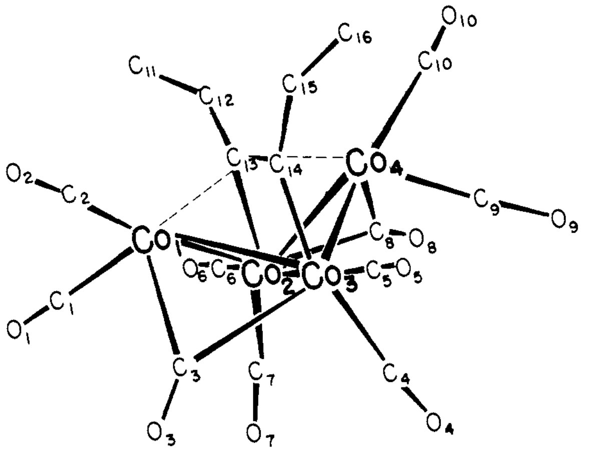


Fig. 1.—Molecular structure of $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$: metal–metal bond distances are Co_1–Co_2 = 2.450 Å., Co_1–Co_3 = 2.433 Å., Co_2–Co_4 = 2.438 Å., Co_3–Co_4 = 2.416 Å., and Co_2–Co_3 = 2.552 Å., the non-bonding distance $Co_1 \ldots Co_4$ = 3.547 Å. (all with e.s.d. ±0.005 Å.). The μ-type Co–C (olefin) distances are Co_1–C_{14} = 2.03 Å., Co_4–C_{13} = 2.03 Å., Co_1–C_{13} = 2.18 Å. and Co_4–C_{14} = 2.15 Å.; the average cobalt distance to the midpoint of C_{13}–C_{14} is 1.97 Å. The average Co–C(olefin) σ-bond distance is 2.01 Å. (all Co–C distances with e.s.d. ±0.014 Å.). The olefinic C–C distance is 1.44 Å. (e.s.d. ±0.020 Å.). For the eight terminal carbonyls the Co–C and C–O distances are 1.73 Å. (av.) and 1.18 Å. (av.), respectively. For the two unsymmetrical bridging carbonyls the Co–C distances are 1.84 Å. (av.) to Co_1 and Co_4 and 1.97 Å. av.) to Co_2 and Co_3; the average C–O distance is 1.17 Å. (The e.s.d.'s for Co–CO and C–O distances are ±0.019 Å. and ±0.023 Å., respectively.)

---

[10] A μ-bond is defined[4] as the interaction by direct overlap of σ-orbital of a metal with an electron-donating π-orbital of an unsaturated hydrocarbon. The metal orbital is perpendicular to the nodal plane of the π-orbital.

[11] J. Chatt, G. A. Rowe and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957).

[12] U. Krüerke and W. Hübel, presented at 17th International Congress of Pure and Applied Chemistry, Munich, Sept., 1959; U. Krüerke and W. Hübel, *Chem. Ber.*, **94**, 2829 (1961).

[13] W. R. Busing and H. A. Levy, "A Crystallographic Least Squares Refinement Program for the IBM 704," ORXLS (1959).

[14] W. R. Busing and H. A. Levy, "A Crystallographic Function and Error Program for the IBM 704," ORXFE (1959).

[15] This terminology refers to a localized MO extending over *four* atomic nuclei, each with one available AO. Alternatively, the interaction may be regarded as a *3-centered* localized MO involving one σ-orbital for each of the two cobalts and the one π-orbital for the olefinic moiety which contributes two electrons. A compound having such bonding is electron-deficient.[16]

[16] *Cf.* R. E. Rundle, *J. Phys. Chem.*, **61**, 45 (1957).

[17] P. Corradini, *J. Chem. Phys.*, **31**, 1676 (1959).

[18] N. C. Baenziger, J. R. Doyle and G. F. Richards, "Advances in the Chemistry of the Coordination Compounds," edited by S. Kirschner, The Macmillan Co., New York, N. Y., 1961, pp. 131–138; L. F. Dahl and C. H. Wei, to be presented at 7th ICCC, Stockholm and Uppsala, Sweden, June, 1962.

[19] R. P. Dodge and V. Schomaker, private communication, 1961.

[20] D. A. Brown, *J. Inorg. Nucl. Chem.*, **10**, 39 (1959); **10**, 49 (1959).

[21] E. B. Hunt and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4777 (1951).

Unlike $Co_2(CO)_6(C_6H_5C_2C_6H_5)$,[8] which is prepared from $Co_2(CO)_8$, the formation of $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$ from $Co_4(CO)_{12}$ does not involve a direct substitution of an acetylene for two bridging carbonyls, provided that Corradini's proposed structure[17] for $Co_4(CO)_{12}$ is correct. A two-dimensional X-ray study of $Co_4(CO)_{12}$ by Corradini[17] revealed the cobalts at the vertices of a tetrahedron, but a crystal disorder prevented a completely unambiguous determination of the molecular geometry of the carbonyl groups. Our structural results show that Corradini's model would necessitate molecular reorganization of carbonyl groups during the formation of $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$ from $Co_4(CO)_{12}$, contrary to the predictions of Hübel and co-workers[5a] based on the experimental reaction conditions. Hübel and Krüerke[12] have suggested possible alternative structures for $Co_4(CO)_{12}$, and in this connection structural work on the iridium and rhodium carbonyls is in progress in this laboratory.

We are pleased to acknowledge the use of the computing facilities of NAL at the University of Wisconsin and the financial support of this research by the National Science Foundation (Grant No. 86-3474).

[22] National Science Foundation Fellow.

DEPARTMENT OF CHEMISTRY LAWRENCE F. DAHL
UNIVERSITY OF WISCONSIN
MADISON 6, WISCONSIN DOUGLAS L. SMITH[22]

RECEIVED APRIL 7, 1962

γ-PYRAN

Sir:

Although the chemistry of pyran has been the subject of research for over a century, the parent compounds, α- and γ-pyran, hitherto have remained unknown.[1] Numerous attempts at the synthesis of these compounds resulted either in ring opening or extensive decompositions.[1] We became interested in these heterocyclic compounds during the course of our synthetic studies on oxepin. We now wish to submit final evidence for the existence of unsubstituted γ-pyran (I).

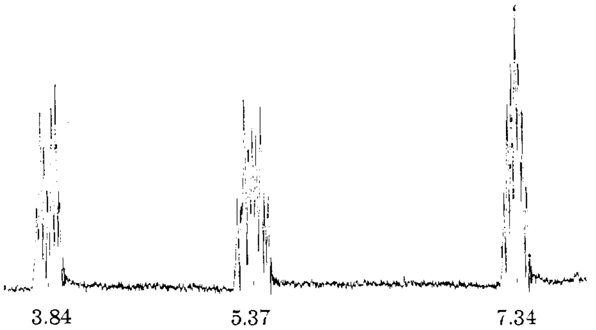
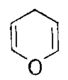
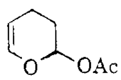


Fig. 1.—The n.m.r. spectrum of γ-pyran in carbon tetrachloride.



I



II

A column (2.5 × 35 cm.) was packed with glass beans (0.5 cm. in diameter) and heated to 350°. 2-Acetoxy-3,4-dihydro-2H-pyran (II)[2] (5 g.) was added dropwise onto the column over a period of 2.5 minutes and the product was trapped in a Dry-Ice cooled flask containing hydroquinone in ether. Nitrogen was used as a carrier gas. Identification of acrolein, vinyl acetate and acetic acid in the reaction mixture indicates that the acetate pyrolysis is competing with the reverse Diels–Alder reaction.[3] Due to the extreme instability of I (*vide infra*) the isolation of I was achieved only by gas chromatography[3] at 50° after treatment of an ethereal solution of the pyrolysis product with wet sodium bicarbonate at 0° for two hours.[4] The yield is 15 or 30% based on starting material consumed. I boils at 84° with slight decomposition.[5]

The chemical proof for the structure of I was obtained by i) the conversion of I to tetrahydropyran[3,6] by catalytic hydrogenation and ii) the preparation of glutaraldehyde bis-dinitrophenylhydrazone[7] from I (m.p. and m.m.p., 186–188°).

Spectral evidence for structure I is given below. The n.m.r. spectrum is very similar to that of 1,4-dihydropyridine[8] and shows one kind of aliphatic and two kinds of olefinic hydrogens, each having an equal intensity. Spin–spin coupling constants are: $J_{34} \simeq 3.0$ c.p.s., $J_{24} \simeq 1.5$ c.p.s.[9] This eliminates α-pyran as a possible structure. The infrared spectrum (chloroform) is simple: 3.28μ (m), 3.42 (m), 3.52 (m), 5.93 (s), 6.12 (s), 7.98 (s), 8.90 (m), 9.36 (s), 9.90 (m), 10.23 (m), 10.40 (m), 11.02 (s) and 11.38 (m). The two bands (5.93, 6.13) in the double bond region are believed to correspond in nature to a doublet observed for an acid anhydride.[10] Only a strong end absorption was observed in the ultraviolet spectrum (methanol).

---

[1] For instance, see: A. Albert, "Heterocyclic Chemistry," Essential Books, Fair Lawn, N. J., 1959, p. 265; N. Campbell, "Chemistry of Carbon Compound," Vol. IVB, ed. by E. H. Rodd, Elsevier Publishing Co., Amsterdam, 1959, Chap. VIII; J. Fried, "Heterocyclic Compound," Vol. I, ed. by R. C. Elderfield, John Wiley & Sons, Inc., New York, N. Y., 1950, Chap. 7.

[2] C. W. Smith, D. G. Norton and S. A. Ballard, *J. Am. Chem. Soc.*, **73**, 5270 (1951); R. H. Snyder, H. J. Shine, K. A. Leibbrand and P. O. Tawney, *ibid.*, **81**, 4299 (1959).

[3] Gas chromatography and infrared spectra were employed for identification of the liquid compounds described in this Communication. Gas chromatography was operated with a 9 mm. × 15-cm. column containing 10% Apiezon L on Anakrom ABS (80–90 mesh). Column conditions were: temperature, 50°; helium flow rate, 45 ml./min. Relative retention times are: acetic acid (1.000), acrolein (0.225), vinyl acetate (0.544), γ-pyran (1.820) and tetrahydropyran (2.499).

[4] This treatment removed most of the acrolein and vinyl acetate as well as acetic acid.

[5] Determined by the Emich method, A. I. Vogel, "Practical Organic Chemistry," 3rd Ed., Longmans, Green and Co., London, 1957, p. 86. A sample in a capillary was introduced in a preheated bath.

[6] D. W. Andrus and J. R. Johnson, "Organic Syntheses," Vol. 23, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 90.

[7] M.p. 186–187° was reported by R. H. Hall and B. K. Howe, *J. Chem. Soc.*, 2480 (1951), and 189–190° and 192° in ref. 3.

[8] M. Saunders and E. H. Gold, *J. Org. Chem.*, **27**, 1439 (1962).

[9] The n.m.r. spectrum was taken with a Varian Associates 60-Mc high resolution spectrometer.

[10] The nature of this splitting has not been thoroughly understood: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 127–128. Divinyl ether and its homologs show similar doublets, A. Kirrmann and P. Chancel, *Bull. Soc. Chim. France*, 1338 (1954).