demonstrate a dramatic enhancement of phenyl migration by the *gem*-dimethyls and point out the importance of the structure of the nonmigrating group in migratory aptitude studies.

Acknowledgment. We thank Professor J. C. Dalton and Mr. James Snyder of the University of Rochester and Professor Alan Waggoner of Amherst College for help in determining the singlet lifetimes, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

References and Notes

(1) See, e.g., (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Close, *J. Am. Chem. Soc.*, **87**, 1410 (1965); (b) H. Kristinsson and G. W. Griffin, *ibid.*, **88**, 378 (1966); (c) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965); (d) S. S. Hixson, *ibid.*, 1155 (1972); (e) P. H. Mazzocchi, and R. C. Ladenson, private communication; (f) H. E. Zimmermann and J. A. Pincock, *J. Am. Chem. Soc.*, **95**, 2957 (1973).

(2) (a) S. S. Hixson, *J. Am. Chem. Soc.*, **94**, 2507 (1972); (b) S. S. Hixson and T. P. Cutler, *ibid.*, **95**, 3032 (1973). The quantum yields shown in Table I of this reference are 0.0010, 0.0026, and <0.0001. The factor of 10^{-3} in front of ϕ_r in this column should not be there; (c) S. S. Hixson, *J. Chem. Soc., Chem. Commun.*, 515 (1975).

(3) (a) There have been several cases involving intramolecular comparisons of photochemical migratory aptitudes.[1c–e,4] However, these studies have not afforded a true measure of relative migratory abilities since in each case the nonmigrating moiety would be different depending on which species migrated. Furthermore, in general only one group migrated so that only an upper limit of migratory aptitudes (with the previous qualification) was obtained. (b) In one intermolecular comparison of methyl and hydrogen migratory abilities in which the nonmigrating group was the same, only quantum yields, not rates, were determined. See the discussion in ref 4a.

(4) (a) See, e.g., K. A. Burdett, F. L. Shenton, D. H. Yates, and J. S. Swenton, *Tetrahedron*, **30**, 2057 (1974); (b) K.-W. Shen, W. E. McEwen, and A. P. Wolf, *Tetrahedron Lett.*, 827 (1969); (c) C. B. Jones and V. Jones, *J. Am. Chem. Soc.*, **89**, 1880 (1967).

(5) E. W. Valyocsik and P. Sigal, *J. Org. Chem.*, **36**, 66 (1971).

(6) (a) L. L. Miller and R. F. Boyer, *J. Am. Chem. Soc.*, **93**, 650 (1971), and references therein; (b) J. A. Berson and M. R. Willcott, *ibid.*, **88**, 2494 (1966).

(7) P. M. Crosby and K. Salisbury, *J. Chem. Soc., Chem. Commun.*, 477 (1975).

(8) H. E. Zimmermann and R. D. Little, *J. Am. Chem. Soc.*, **96**, 5143 (1974).

(9) Zimmermann[10] has presented strong arguments that bridging is rate limiting in the divinylmethane version of the di-π-methane reaction.

(10) H. E. Zimmermann, D. P. Werthemann, and K. S. Damm, *J. Am. Chem. Soc.*, **96**, 439 (1974).

(11) (a) Using $\phi_{f(1a)} = 0.155$ (ref 7), we calculate from the data in the table that $k_{f(1a)} = 1.6 \times 10^7\ s^{-1}$ ($k_{d(1a)} = 8 \times 10^7\ s^{-1}$) while $k_{f(3)} = 2.1 \times 10^7\ s^{-1}$, a difference of 31%. (b) If the sum $k_f + k_d$ for **3** is 30% larger than that for 1**a** or **1b** then $k_r'_{(3)} = 3 \times 10^7\ s^{-1}$. (c) The maximum possible value of $k_r'_{(3)}$ is found by assuming $1/\tau_{s(3)} = k_f + k_r'$, i.e., that k_d is negligible; $k_r'_{(3)max} = 1.4 \times 10^8\ s^{-1}$.

(12) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, p 196.

Stephen S. Hixson
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01002

Received May 19, 1975

Tris(η^5-cyclopentadienyl)tricarbonyltricobalt. An Exceptionally Deformable Molecule

Sir:

Stereochemical nonrigidity has been widely investigated in a variety of compounds in recent years using NMR spectroscopy.[1] While in most cases the barriers to the intramolecular rearrangements responsible for the nonrigidity have been in the range of 8–20 kcal/mol, there are a few cases in which the barriers are much lower. Of particular interest is the type of molecule in which there is a continuous range of configurations over which the free energy changes by only a few kilocalories, so that many, or even a virtually continuous range, of molecular configurations may coexist in solution. An example already known is $Fe_3(CO)_{12}$.[2,3] Another such readily deformable molecule, a type for which we propose the designation *fictile*, is reported here.

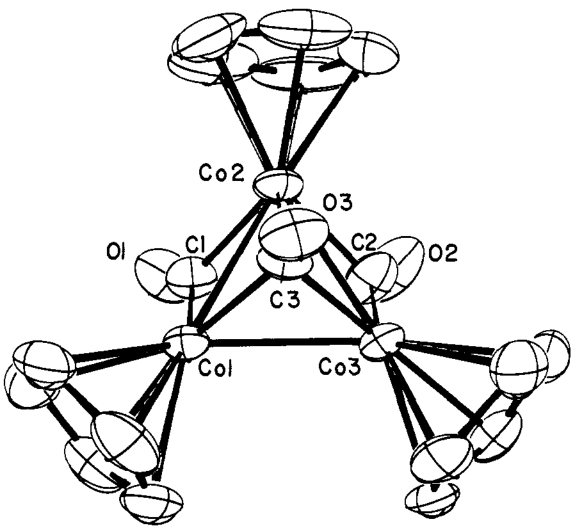


Figure 1. An ORTEP drawing of the $[\eta^5\text{-}C_5H_5)Co(CO)]_3$ molecule as it occurs in the crystal.

Table I. Summary of Pertinent Bond Lengths and Angles of $[CpCo(CO)]_3$

Col–Co2	2.440 (4) Å	Co2–C1	1.99 (3) Å
Co2–Co3	2.458 (4) Å	Co2–C2	2.11 (4) Å
Col–Co3	2.521 (4) Å	∠Col–C1–01	148.6 (7)°
Col–C1	1.78 (3) Å	∠Co3–C2–02	153.2 (7)°
Co3–C2	1.75 (4) Å		

As part of our current effort to prepare organometallic complexes containing metal-metal multiple bonds,[4] we have attempted to prepare compounds of the type $CpCo(\mu\text{-}R_2C_2)CoCp$ which would be expected to contain a cobalt-cobalt double bond by the photochemical reaction of $CpCo(CO)_2$ and di-*tert*-butylacetylene, $t\text{-}Bu_2C_2$. This reaction did not produce the desired $Cp_2Co_2(\mu\text{-}t\text{-}Bu_2C_2)$, but did provide $[CpCo(CO)]_3$ a substance earlier reported by King.[5] The inability of Uchtman and Dahl[6] to reproduce King's synthesis coupled with the recently reported work of Vollhardt et al.[7] who, along with King, have proposed incorrect structures for $[CpCo(CO)]_3$ prompted us to report a few results of our structural and spectral studies on this and related systems. A full report will appear later.

$[CpCo(CO)]_3$ crystallizes in the triclinic space group, $P\bar{1}$, with cell dimensions: $a = 9.128$ (4), $b = 11.691$ (5), $c = 7.948$ (4) Å; $\alpha = 105.45$ (4)°, $\beta = 100.70$ (4)°, $\gamma = 91.21$ (3)°. The structure, shown in Figure 1, was solved using 2738 reflections having $F_o^2 > 3\sigma(F_o^2)$ and $2\theta < 50°$. Data were collected at 21 ± 2 °C with monochromatized Mo Kα radiation using θ-2θ scans. Presently the structure is refined to convergence using isotropic temperature parameters for all non-hydrogen atoms; the conventional R value is 9.4%.

The structure of $[CpCo(CO)]_3$, like that of Uchtman and Dahl's $Cp_3Co_3(\mu_3\text{-}CO)$ (μ_3-O), is based upon a triangle of cobalt atoms each of which is bonded to a η^5-cyclopentadienyl ring, and it also contains a triply bridging carbonyl, C3-O3 (Figure 1). In addition $[CpCo(CO)]_3$ contains two semibridging carbonyls.[3,8] That Cl-O1 and C2-O2 are indeed semibridges can be seen from the data summarized in Table I: Cl is 0.21 Å closer to Col than to Co2 while C2 is 0.36 Å closer to Co3 than Co2; these data together with the very low M-C-O angles clearly indicate the marked asymmetry of these carbonyl bridges.

In contrast to the equilateral triangle of cobalt atoms found in $Cp_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$, the cobalt atoms of

Table II. Infrared Spectra of $[CpCo(CO)]_3$[a]

Nujol	1833, 1775, 1673
THF	1958 (s), 1843 (m), 1805 (s), 1760 (s), 1702 (m)
$CHCl_3$	1959 (s), 1840 (m), 1797 (m), 1750 (m), 1710 (w)
C_6H_6	1959 (s), 1811 (s), 1753 (m)

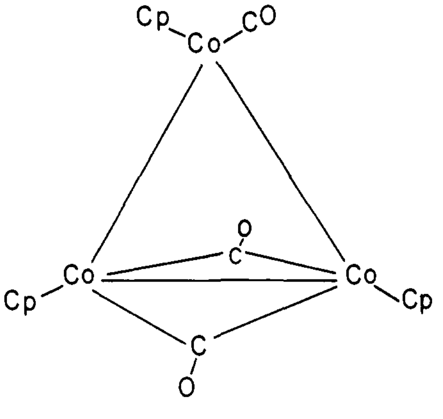
[a] Spectra in cm^{-1} recorded on a Perkin-Elmer 267 spectrometer and calibrated with polystyrene

$[CpCo(CO)]_3$ form an isosceles triangle with the two distinct cobalt-cobalt bond lengths of 2.521 Å (Co1-Co3) and 2.449 Å (average of Co1-Co2 and Co2-Co3). The molecule has approximate C_S-m symmetry (though no crystallographic symmetry is imposed) with the minor plane passing through Co2, C3, O3, and bisecting the Co1-Co3 bond. Though the cobalt-cobalt bond lengths of $[CpCo(CO)]_3$ vary from 2.440 to 2.521 Å, this variation is well within the range found for other reported cobalt-cobalt single bonds: 2.365 Å, $Cp_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$;[6] 2.463 Å, $(t\text{-}Bu_2\text{-}C_2)Co_2(CO)_6$;[9] and 2.457-2.527 Å, $Co_4(CO)_{12}$.[10]

The solid-state infrared spectrum of $[CpCo(CO)]_3$, 1833, 1775, and 1673 cm^{-1}, (cf. 1835, 1775, and 1675 cm^{-1} reported by Vollhardt et al.[7]) is readily interpreted in terms of the structure reported here. The 1673-cm^{-1} band is assigned to the C-O stretch of the triply bridging CO while the 1833- and 1775-cm^{-1} bands can be assigned to symmetric and antisymmetric stretching modes of the semibridging CO's. The solid-state infrared spectrum is somewhat dependent upon what solvent was used for crystallization in that peaks corresponding to King's "second isomer" may or may not be present. However, we feel that in light of the apparent ease with which the positions of the CO ligands can be changed, vide infra, this "second isomer" is basically the same as the structure reported here but with only slight changes in the three CO positions.

Infrared spectra of $[CpCo(CO)]_3$ recorded in solution are vastly different and vary markedly from one solvent to another, as shown in Table II.

For example, in benzene the infrared spectrum of $[CpCo(CO)]_3$ exhibits three bands: 1959, 1811, and 1753 cm^{-1}. These bands are indicative of structure **1**, whose rhodium analogue[11] has been characterized by x-ray crystallography and infrared spectroscopy (KBr: 1973, 1827, 1794, and 1744 cm^{-1}). Furthermore the infrared spectra (both in solution and in the solid state) of the methylcyclopentadienyl analogue, $[Me\text{-}Cp)Co(CO)]_3$, exhibits three bands at 1957 ± 4, 1843 ± 5, and 1800 ± 6 cm^{-1}) which are again consistent with **1**.



1

It appears that the geometry of the three CO ligands relative to the central triangle of metal atoms in complexes of the type, $[CpM(CO)]_3$(M = Co, Rh[11,12]), is very sensitive to subtle changes in the environment of the molecule (e.g., solid state vs. solution, polarity of solvent, etc.). We propose that molecules of such extraordinary deformability or plasticity be designated *fictile* molecules.

Further chemical, spectroscopic, and structural studies on this and related systems are now in progress. A full account of the structure of $[CpCo(CO)]_3$ together with the results of all of our spectroscopic and chemical studies will be the subject of a future paper.[13]

References and Notes

(1) "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975.
(2) F. A. Cotton and D. L. Hunter, *Inorg. Chim. Acta*, **11**, L9 (1974).
(3) F. A. Cotton, *Prog. Inorg. Chem.*, **21**, 1 (1976).
(4) F. A. Cotton, J. D. Jamerson, and B. R. Stults, *J. Organomet. Chem.*, **94**, C53 (1975).
(5) R. B. King, *Inorg. Chem.*, **5**, 2227 (1966).
(6) V. A. Uchtman and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 3763 (1969).
(7) K. P. C. Vollhardt, J. E. Bercaw, and R. G. Bergman, *J. Organomet. Chem.*, **97**, 283 (1975).
(8) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 1233 (1974).
(9) F. A. Cotton, J. D. Jamerson, and B. R. Stults, *J. Am. Chem. Soc.*, in press.
(10) F. H. Carre, F. A. Cotton, and B. A. Frenz, *Inorg. Chem.*, in press.
(11) E. F. Paulus, E. O. Fischer, H. P. Fritz, and H. Schuster-Woldan, *J. Organomet. Chem.*, **10**, P3 (1967).
(12) E. F. Paulus and O. S. Mills, *J. Organomet. Chem.*, **10**, 331 (1967).

(13) This work was supported by The Robert A. Welch Foundation (Grant No. A494) and by the National Science Foundation (Grant No. MPS72-04536-A03).

F. Albert Cotton,* Jackie D. Jamerson
Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received October 6, 1975

Nonspecific Biosynthesis of Hopane Triterpenes in a Cell-Free System from *Acetobacter rancens*

Sir:

3-Desoxytriterpenes of the hopane family are ubiquitous constituents of sedimentary organic matter (including petroleums, coals, shales, muds, etc.).[1] They are also present in many procaryotic microorganisms, blue-green algae or bacteria.[2] We have studied one aspect of their biosynthesis, namely, the use of a cell-free system derived from an *Acetobacter;* this has revealed a novel type of enzyme-mediated reaction, with an unusually low degree of substrate selectivity but a high degree of product specificity.

The immediate precursor of 3-desoxytriterpenes has been shown in two instances to be squalene **1**, and not squalene 2,3-epoxide **2**; this is the course of the biosynthesis of tetrahymanol in a protozoan, *Tetrahymena pyriformis*,[3] and of the biosynthesis of fern-7-ene in a fern, *Polypodium vulgare*.[4]

We have therefore incubated [12,13-^{3}H]squalene (6 × 10^6 dpm) with a system obtained from cells of *Acetobacter rancens* (strain NCIM 6249), disrupted by ultrasound treatment in a phosphate buffer (pH 7.4).

The expected cyclization products, hop-22(29)-ene (**3**) and hopan-22-ol (**6**), were added as carriers to the organic extract and reisolated by thin-layer chromatography on silica gel. Constant specific radioactivity was achieved after one recrystallization, and maintained through three more.

The two substances identified in this way were furthermore converted to derivatives. Hop-22(29)-ene **3** gave 29-acetoxyhopane **9** by hydroboration, oxidation with hydrogen peroxide, and acetylation; hopan-22-ol **6** gave hop-21-ene **12** by dehydration with phosphorus oxychloride and pyridine. These two derivatives were themselves purified to constant specific radioactivity, reached after one recrystallization and maintained through three more.