

H at 5.95 τ (2.8); CH₂ groups and ethyl CH₃ at 8.05, 8.28 and 8.87 τ (8.8). The infrared spectrum in CCl₄ shows N-H at 3454 cm.⁻¹ (sharp) and 3348 cm.⁻¹ (hydrogen bonded, broad); olefinic C-H at 3030 cm.⁻¹; CO at 1720 cm.⁻¹; double bond at 1648 cm.⁻¹. Urethane (VIII) was identified by comparison of its infrared spectrum and its vapor phase chromatography retention time with those of an authentic sample.

N-Carboethoxyazepine was obtained in 50% of the theoretical yield from a homogeneous solution of (VI) in benzene and 1.1 equivalents of triethylamine. It was identified by its ultraviolet spectrum (λ_{\max} at 210 m μ ($\log \epsilon$ 4.37) and λ_{\max} 329 m μ ($\log \epsilon$ 2.74)), its infrared spectrum (no NH; H-H at 3051, 3033, 2984, 2933 cm.⁻¹; CO at 1717 cm.⁻¹, double bonds at 1651 cm.⁻¹), its n.m.r. spectrum (triplet at 8.71 τ ; quartet at 5.81 τ ; multiplet from 3.9 to 4.8 τ). It was also hydrogenated² to the hexahydro compound, the infrared spectrum of which was identical with that of a sample prepared from hexamethyleneimine and ethyl chloroformate. The formation of phenylurethane in the nitrene reaction could not be proven, since N-carboethoxyazepine itself readily isomerizes to phenylurethane.

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STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

WALTER LWOWSKI
TOM J. MARICICH
THOMAS W. MATTINGLY, JR.

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Rh₆(CO)₁₆ AND ITS IDENTITY WITH PREVIOUSLY REPORTED Rh₄(CO)₁₁

Sir:

A three-dimensional crystal structure investigation has shown that the compound previously analyzed as Rh₄(CO)₁₁¹ has the molecular formula Rh₆(CO)₁₆.

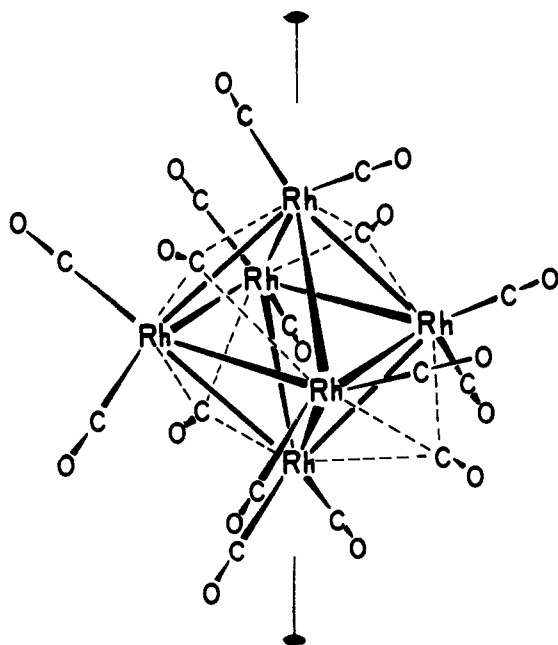


Fig. 1.—Molecular structure of Rh₆(CO)₁₆.

This is the first example of a hexanuclear metal carbonyl.

Crystals of this air-stable black rhodium carbonyl were prepared by the reaction of dry RhCl₃ and silver or copper powder at 80–230° and 200 atmospheres of carbon monoxide.¹ Rh₆(CO)₁₆ crystallizes in a mono-

(1) W. Hieber and H. Lagally, *Z. anorg. allgem. Chem.*, **251**, 96 (1943).

clinic unit cell of symmetry I2/a with dimensions $a = 17.00 \pm 0.03$ Å., $b = 9.78 \pm 0.02$ Å., $c = 17.53 \pm 0.03$ Å., $\beta = 121^\circ 45' \pm 30'$. The observed density of 2.87 g./cc. determined by the flotation method agrees well with the calculated density of 2.86 g./cc. based on four Rh₆(CO)₁₆ molecules per unit cell.

The structure was determined from an analysis of three-dimensional intensity data taken photographically with MoK α radiation. Final least-squares refinement² with an isotropic temperature factor for each atom gave discrepancy factor $R_1 = 7.1\%$ and $R_2 = 7.6\%$.

In each molecular unit (Fig. 1) the rhodium atoms are located at the corners of an octahedron with a weighted average metal-metal bonding distance of $2.776 \pm 0.001_4$ Å. Twelve of the sixteen carbonyl ligands are terminal groups while the remaining four are located on 3-fold axes above four of the octahedral faces. Each of these latter four carbonyls which are directed toward the vertices of a tetrahedron is bonded to three rhodium atoms. The eight-coordinated tetragonal antiprismatic rhodium atoms each have the same localized ligand environment: four adjacent rhodium atoms, two terminal carbonyl groups and two of the carbonyls that bridge three metal atoms. The idealized molecular point group symmetry is T_d-43m. One of the three molecular 4 axes lies on a crystallographic 2-fold axis. The following weighted average bond distances are found: for the terminally bonded carbonyls, Rh-C = 1.864 ± 0.015 Å., C-O = 1.155 ± 0.015 Å.; for the carbonyls bonded to three metal atoms, Rh-C = 2.168 ± 0.012 Å., C-O = 1.201 ± 0.022 Å.

This is the first known polynuclear metal carbonyl that contains carbonyls bridged to three metal atoms. Similarly bridged groups have been shown conclusively by X-ray diffraction³ for (C₆H₅)₃Ni₃(CO)₂ in agreement with its infrared spectrum.⁴ A comparison of angles involving the bridge carbonyls in (C₆H₅)₃Ni₃(CO)₂ and Rh₆(CO)₁₆ shows close agreement: Ni-C-O angle = 134° vs. Rh-C-O angle = 132° (av.); Ni-C-Ni angle = 77° vs. Rh-C-Rh angle = 79.5° (av.). Carbonyl ligands bonded to triangular arrangements of metal atoms have been predicted from infrared data for (C₆H₅)₃CO₃(CO)₂¹⁺,^{3,5,6} and (C₇H₅)₃CO₃(CO)₂¹⁺,⁶ and by analogy for Fe₃(CO)₁₁^{2-3,7}

Octahedral arrangements of metal atoms similar to that in Rh₆(CO)₁₆ are found in the cations Mo₆Cl₈^{4+,8} Nb₆Cl₁₂^{2+,9} Ta₆Cl₁₂^{2+,9} and Ta₆Br₁₂^{2+,9} all of which can also be described on the basis of a tetragonal antiprismatic arrangement¹⁰⁻¹² of eight electron pairs about each metal atom.¹³

(2) W. R. Busing and H. A. Levy, "A Crystallographic Least-Squares Refinement Program for the IBM 704," Oak Ridge National Laboratory Report 59-4-37 (1959).

(3) A. A. Hock and O. S. Mills, "Advances in the Chemistry of the Coordination Compounds," edited by S. Kirschner, The Macmillan Co., New York, N. Y., 1961, pp. 640-648.

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(5) E. O. Fischer and O. Beckert, *Angew. Chem.*, **70**, 744 (1958).

(6) P. Chini and R. Ercoli, *Gazz. chim. ital.*, **88**, 1171 (1959).

(7) W. Hieber and G. Brendel, *Z. anorg. allgem. Chem.*, **259**, 324 (1957).

(8) C. Brosset, *Arkiv Kemi, Mineral. Geol.*, **20A**, No. 7 (1945); **23A**, No. 11 (1946); C. Brosset, *Arkiv Kemi*, **1**, 353 (1950); P. A. Vaughan, *Proc. Natl. Acad. Sci. U.S.A.*, **36**, 461 (1950).

(9) P. A. Vaughan, J. H. Sturdivant and L. Pauling, *J. Am. Chem. Soc.*, **72**, 5477 (1950); R. B. Corey, R. H. Stanford, Jr., R. E. March, Y. C. Leung and L. M. Kay, *Acta Cryst.*, **15**, 1157 (1962).

(10) G. H. Duffey, *J. Chem. Phys.*, **19**, 963 (1951).

(11) R. J. Gillespie, *Can. J. Chem.*, **39**, 2336 (1961); R. J. Gillespie, in ref. 3, pp. 34-49.

(12) L. D. Crossman, D. P. Olsen and G. H. Duffey, *J. Chem. Phys.*, **38**, 73 (1963).

(13) The two rhodium-bridged carbonyl bonds presumably are "bent." Directed valence bond metal hybrid orbitals have been constructed by Duffey for both a regular tetragonal antiprismatic arrangement¹⁴ and a distorted version¹⁰ based on the Ta₆Cl₁₂²⁺ structure.

(14) C. H. Duffey, *J. Chem. Phys.*, **18**, 746 (1950).

$\text{Rh}_6(\text{CO})_{16}$ is an exception to the "inert gas rule" for the polynuclear metal carbonyls in that the entire molecule contains two electrons in excess of the "xenon" configuration for each rhodium atom. The observed spin-pairing of all electrons¹⁵ can be rationalized from a consideration of LCAO MO symmetry arguments based on an assumed localized D_{4d} antiprismatic configuration. Sixteen of the $18^{1/3}$ electrons per rhodium are utilized in filling the eight σ -bonding orbitals.¹⁷ The problem then resolves into placing the remaining $2^{1/3}$ electrons per rhodium (or seven electron-pairs for the six rhodiums) into appropriate antibonding MO's which are assumed to possess mainly the characteristics of the metal AO's. From the presumed energetics of the tetragonal antiprismatic system,¹⁸ the rhodium-like orbitals available for bonding with one another are the lowest-lying d_{z^2} and the next lowest degenerate ($d_{x^2-y^2}$, d_{xy}) MO's. From the d_{z^2} orbitals for the six rhodiums one can form six linear combinations which under octahedral (O_h) symmetry split to give a_{1g} , e_g and t_{1u} levels. Since the d_{z^2} orbital for each rhodium apparently lies considerably below the other orbitals due to its antiprismatic environment, it is reasonable that all of these levels are occupied with six electron-pairs. Likewise, the six $d_{x^2-y^2}$ orbitals give rise to a_{2g} , e_g and t_{2u} and the six d_{xy} orbitals yield a_{2u} , e_u and t_{2g} . From overlap considerations it appears that the lowest of these six energy levels is the a_{2u} , and hence the remaining electron-pair will occupy a non-degenerate level. Since this electron-pair is strongly delocalized and has low-lying excited levels, both the spin-pairing and the intense absorption of this black compound can be explained. Of obvious significance is whether these two electrons can be selectively removed to give $\text{Rh}_6(\text{CO})_{16}^{1+}$ and $\text{Rh}_6(\text{CO})_{16}^{2+}$ species.

It should be noted that the unpaired electron in $(\text{C}_6\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ which also formally must lie in an antibonding MO with respect to the $\text{C}_6\text{H}_5^{1-}$ and CO ligands has been assigned on the basis of electron spin measurements¹⁹ to a π -bonding combination of essentially 3d orbitals on the nickel atoms. For $\text{Rh}_6(\text{CO})_{16}$, however, the antibonding π -type (d_{xz} , d_{yz}) MO's for a tetragonal antiprismatic arrangement appear to be energetically unfavorable and furthermore, a combination of such orbitals under octahedral symmetry would lead to a lowest-lying degenerate "spin-free" state. It then would be necessary to invoke the Jahn-Teller theorem to obtain a "spin-paired" electronic configuration in the ground state. Within experimental error no molecular distortion is observed.

The molecular structure is in complete accord with the observed infrared spectrum²⁰ which shows two bands in the terminal carbonyl region at 2073 and 2026 cm^{-1} and one band at 1800 cm^{-1} which may be assigned to the bridged carbonyls each bonded to three rhodium atoms. A vibrational analysis reveals that the T_d structure predicts two infrared-active terminal C-O

(15) Magnetic susceptibility measurements¹⁵ on $\text{Rh}_6(\text{CO})_{16}$ show that it is very slightly paramagnetic. The susceptibility is not field dependent and shows no change on cooling from room temperature to 90°K. Since a value of 0.29×10^{-6} e.m.u./g. is obtained, it is concluded that there are no free spins and that the observed paramagnetism comes from small orbital contributions.

(16) We wish to thank Drs. F. J. Darnell and D. Flippin of the Central Research Department, E. I. du Pont de Nemours and Co., for carrying out this study for us.

(17) Each rhodium possesses a ninth orthogonal valence σ -type orbital made up primarily of the d_{z^2} AO which is directed along a 4-axis of $\text{Rh}_6(\text{CO})_{16}$ toward the center of the molecule. The degenerate (d_{xz} , d_{yz}) AO's are π -type orbitals while the degenerate ($d_{x^2-y^2}$, d_{xy}) AO's are δ -type orbitals (referred to the principal symmetry axis).

(18) Cf., J. R. Perumareddi, A. D. Liehr and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963).

(19) H. C. Longuet-Higgins and A. J. Stone, *Mol. Physics*, **5**, 417 (1962).

(20) W. Beck and K. Lottes, *Chem. Ber.*, **94**, 2578 (1961).

stretching frequencies (both of F_2 symmetry) and one infrared-active asymmetric bridge C-O stretching frequency (F_2 symmetry). As assignment also can be made with the assumption that the coupling between the terminal carbonyl groups attached to different rhodium atoms can be neglected. Each $\text{Rh}(\text{CO})_2$ fragment of localized C_{2v} symmetry would then give rise to two infrared-active terminal C-O stretching fundamentals of A_1 and B_1 representation; the symmetric mode (A_1) should correspond to the higher frequency (i.e., 2073 cm^{-1}) and the antisymmetric mode (B_1) to the lower frequency (i.e., 2026 cm^{-1}).^{21,22}

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON 6, WISCONSIN
ANORGANISCH-CHEMISCHES LABORATORIUM
TECHNISCHE HOCHSCHULE MÜNCHEN
MÜNCHEN 2, GERMANY

EUGENE R. COREY
LAWRENCE F. DAHL

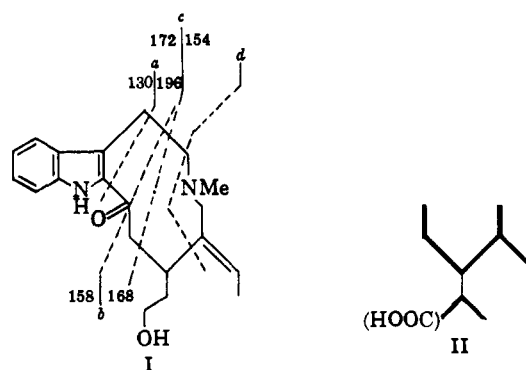
WOLFGANG BECK

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BURNAMICINE, A CRYPTOPINE-LIKE ANALOG OF CORYNANTHEOL

Sir:

The alkaloids of *Hunteria eburnea* Pichon have been the subject of a detailed examination^{1,2} and have yielded 23 bases, among which were discerned representatives of new classes of indole alkaloids, in particular the eburnamine group³ and the quaternary diastereoisomeric N_b -methyl derivatives of hunterburnine.⁴ Although several examples of yohimbine bases were found in the quaternary base fraction,^{1,4} none were recognized until now among the tertiary bases,² and the results to be described below allow us to put forward the structure I for burnamicine,² making it not



only the equivalent in indole alkaloids of cryptopine in isoquinoline alkaloids, but also the first representative of yet another variant of the formal yohimbine precursor II.⁵ This knowledge may be of importance

(1) M. F. Bartlett, B. Korzun, R. Sklar, A. F. Smith and W. I. Taylor, *J. Org. Chem.*, in press.

(2) M. F. Bartlett, R. Sklar, A. F. Smith and W. I. Taylor, in preparation.

(3) M. F. Bartlett and W. I. Taylor, *J. Am. Chem. Soc.*, **82**, 5941 (1960).

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