

the same type of M-H bonding in the three compounds. It thus appears that some earlier views¹⁹ on metal-hydrogen bond character in unsubstituted carbonyl hydrides may need to be modified.²⁰

(19) (a) F. A. Cotton and G. Wilkinson, *Chem. Ind. (London)*, 1305 (1956); (b) F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 4425 (1958); (c) E. O. Bishop, J. L. Down, P. R. Emtage, R. E. Richards, and G. Wilkinson, *J. Chem. Soc.*, 2484 (1959) [this paper summarizes much of the discussion on carbonyl hydrides].

(20) A theoretical study proposing a normal covalent distance for Co-H in CoH(CO)₃ has been recently reported: R. M. Stevens, C. W. Kerns, and W. M. Lipscomb, *J. Chem. Phys.*, **37**, 279 (1962); see also L. L. Lohr, Jr., Ph.D. Thesis, Harvard University, 1963.

(21) Deceased November 4, 1962.

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Studies of the Metal-Hydrogen Bond: Structure of HRh(CO)(P(C₆H₅)₃)₃¹

Sir:

We wish to report the determination of the structure, including the Rh-H bond length, of HRh(CO)(P(C₆H₅)₃)₃ (hereafter I). Although the metal-hydrogen bond in transition metal hydride complexes has been the subject of both speculation and controversy,^{2,3} it has not been the object of many definitive experiments.⁴ This is probably because the unsubstituted parent compounds, such as HCo(CO)₄, are unstable, and because the substituted stable compounds, such as I, are not generally suitable for the direct study of the metal-hydrogen bond.

Bath and Vaska⁵ have shown spectroscopically that the metal-hydrogen bond in I (and in the analogous Ir compound) is probably very similar to the controversial one in HCo(CO)₄. Because of this and because in fact I is favorable for an X-ray study of a metal-hydrogen bond, we undertook a detailed study of the structure. We find the Rh-H bond length to be 1.72 ± 0.15 Å., and hence to be "normal" as judged by the usual radii sum rules. The arguments of Cotton and others² in support of very short metal-hydrogen bonds (<1.2 Å.) may thus need re-examination.⁶

Crystals of I, kindly supplied by L. Vaska and prepared in the manner described by Bath and Vaska,⁵ belong to the monoclinic system; space group C_{2h}⁵-P2₁/n, with four molecules in a cell of dimensions *a* = 10.11 ± 0.05, *b* (unique axis) = 33.31 ± 0.15, *c* = 13.33 ± 0.07 Å., β = 90.0 ± 0.1° (ρ_c = 1.36, ρ₀ = 1.33 g./cm.³). No symmetry conditions are imposed on the molecule. Multiple-film integrated Weissenberg data collected at room temperature with Cu Kα radiation were estimated visually.

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) F. A. Cotton and G. Wilkinson, *Chem. Ind. (London)*, 1305 (1956); (b) F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 4425 (1958); (c) E. O. Bishop, J. L. Down, P. R. Emtage, R. E. Richards, and G. Wilkinson, *J. Chem. Soc.*, 2484 (1959) [this paper summarizes much of the discussion of the hydrogen position in transition metal carbonyl hydrides].

(3) R. M. Stevens, C. W. Kern, and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 279 (1962).

(4) All that is actually known is from a broad-line n.m.r. study of H₂Fe(CO)₄²⁰ where, on the assumption of a pure sample and the absence of intermolecular effects, the H-H distance is found to be 1.88 ± 0.05 Å. There is the undocumented claim by M. J. Bennett, M. Gerloch, J. A. McCleverty, and R. Mason (*Proc. Chem. Soc.*, 357 (1962)) that from two-dimensional X-ray data they have determined the Mo-H distances in (C₆H₅)₂MoH₂ to be 1.1 ± 0.2 Å.

(5) S. S. Bath and L. Vaska, *J. Am. Chem. Soc.*, **85**, 3500 (1963).

(6) It has already been shown that for HCo(CO)₄² and other transition metal hydride complexes [L. L. Lohr, Jr., and W. N. Lipscomb, private communication] it is not necessary to postulate an abnormally short metal-hydrogen bond in order to account for the large chemical shift of the proton in these compounds.

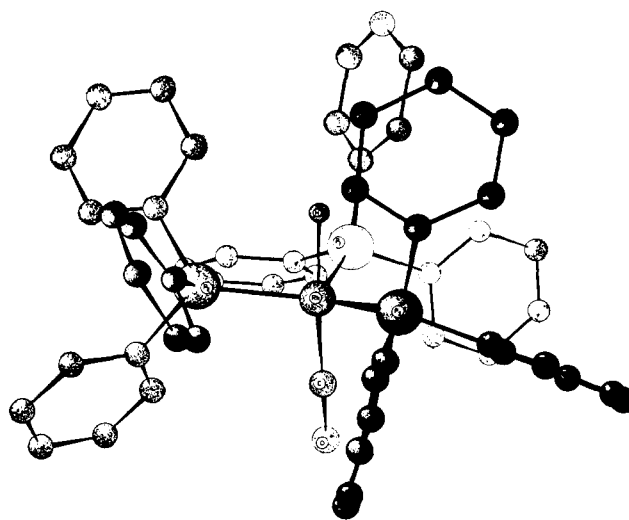


Fig. 1.—A perspective drawing of one molecule of HRh(CO)(P(C₆H₅)₃)₃ as viewed from 40 Å.

Conventional Patterson and Fourier techniques served to locate approximately the 60 atoms (omitting hydrogens) in the asymmetric unit. Isotropic least-squares refinement of these requires the inversion of a matrix of order 240 for each cycle. This impractical number of positional and thermal parameters was reduced to 87 by modification of our version of the Busing-Levy ORFLS program to handle the constraint of the phenyl rings to their well known geometry. Each phenyl ring is described by an isotropic thermal parameter and by the six parameters that relate the center of mass of the ring and the orientation of its internal axial system to the unit cell coordinate system.⁷ The conventional *R* factor at various stages of the calculation was: Rh and P, 34%; isotropic refinement with phenyl groups, 7.9%; final refinement (Rh anisotropic), 7.7%. A difference Fourier calculated at this stage showed no density higher than 0.75 e⁻ Å.³

We were encouraged to attempt to locate the position of the hydride ion for the following reasons: (1) the data are of good quality, both because absorption errors are negligible (μ_{Cu} = 34 cm.⁻¹) and because problems with white radiation are not serious with Cu Kα; (2) owing to the very large cell, there are many useful low-angle data to which the hydride ion contributes; (3) the structure exhibits little thermal motion, presumably because the rigid phenyl rings interlock tightly; (4) the group refinement prevents the loss of detail (admittedly both real and spurious) by eliminating extra, physically unnecessary parameters.⁸ The difference Fourier based on all of the data (cut-off *t*₀ = 0.416 Å.⁻¹, 1650 independent reflections) exhibits a prominent peak at the position expected for the hydride ion (*i.e.*, along the (OC)-Rh line normal to the phosphorus plane, Fig. 1). However, this peak is near to and presumably distorted by a peak that probably arises from a deficiency in our treatment of the Rh scattering or thermal motion. Accordingly a series of difference Fouriers was calculated for decreasing values of *t*₀. The interfering peak, as well as most other peaks, decreased in height and changed position, whereas the hydride peak, the most prominent on the maps, remained at essentially the same position and had

(7) Refinements involving rigid groups have also been described recently by G. Scheringer, *Acta Cryst.*, **16**, 546 (1963).

(8) The success of the group refinement may be judged by the fact that the P-phenyl distances range from 1.79 to 1.87 Å. and average 1.830(22) Å. On the assumption of equivalence this is a reasonable distribution, being consistent with the estimate of a standard deviation of the P-phenyl distance of 0.02 Å. from the least-squares calculations.

the expected height.⁹ The function $G = \sigma(\rho)/\rho_H$, where ρ_H is the hydrogen electron density, exhibits a shallow minimum of approximately 0.21 at $t_0 = 0.25 \text{ \AA}^{-1}$ (460 independent reflections); here the Rh-H distance is 1.72 \text{ \AA}. At $t_0 = 0.30 \text{ \AA}^{-1}$ (761 independent reflections) G is 0.23 and the Rh-H distance is 1.66 \text{ \AA}. At lower values of t_0 , G is substantially higher. The standard deviation in the hydride position at $t_0 = 0.25 \text{ \AA}^{-1}$, as estimated by Cruickshank's method,¹⁰ is 0.15 \text{ \AA}, about 7 times that estimated for the carbonyl C. On the basis of these calculations we feel confident that the Rh-H distance is $1.72 \pm 0.15 \text{ \AA}$.

Figure 1 is a perspective view of the molecule. It has the bipyramidal configuration surmised by Vaska.⁵ The Rh atom lies approximately 0.36 \text{ \AA} below the phosphorus plane toward the carbonyl, and so the CRhP₃ segment is neither tetrahedral nor part of a regular trigonal bipyramid. The Rh-CO distance is normal, and there appears to be no *trans* effect as in HPtX(PR₃)₂ (X = Br,¹¹ Cl¹²) where the Pt-X distance is abnormally long. Table I lists some of the more important distances and angles.

TABLE I

SELECTED DISTANCES AND ANGLES IN HRh(CO)(P(C₆H₅)₃)₃

	Distance, \text{ \AA}		Angle
Rh-H	1.72(15) ^a	Rh-C-O	179(2) ^o
Rh-P	2.337(8)	OC-Rh-H	170(5)
	2.314(7)		
	2.317(7)	P-Rh-CO	94.8(9)
			103.8(8)
Rh-CO	1.81(2)		98.0(9)
C-O	1.18(3)	P-Rh-P	115.8(3)
			120.6(3)
P-phenyl	1.83(2) ^b		116.6(3)
		Phenyl-P-phenyl	101.3(2.1) ^b

^a The numbers in parentheses are estimated standard deviations. ^b Average of the nine phenyl rings.

(9) The experimental heights of the hydride peak are 0.40, 0.34, and 0.20 e/\text{ \AA}^3 at t_0 values of 0.30, 0.25, and 0.20 \text{ \AA}^{-1}. The theoretical heights for a hydride ion undergoing no thermal motion are 0.42, 0.32, and 0.21 e/\text{ \AA}^3. Different assumptions about the charge on the H and about thermal motion do not seriously affect this remarkable agreement.

(10) D. W. J. Cruickshank, *Acta Cryst.*, **7**, 519 (1954), and earlier papers.

(11) P. G. Owston, J. M. Partridge, and J. M. Rowe, *ibid.*, **13**, 246 (1960).

(12) R. Eisenberg and J. A. Ibers, unpublished results.

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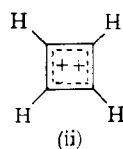
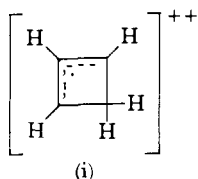
RECEIVED AUGUST 29, 1963

Formation of the Stable 1,3-Dihydroxy-2,4-diphenylcyclobutadiene Dication by Ionization of an α -Bromoketone

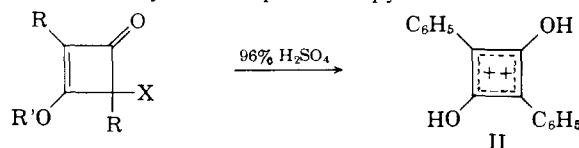
Sir:

Routes to analogs of the cyclobutadiene dication¹ seem to be under active investigation by several groups.²⁻⁴ We wish to report the ionization of the α -

(1) Systematic nomenclature of such dicarbonium ions presents a problem.²⁻⁴ It seems to us that the name "cyclobutenyl dication"¹ implies structure (i), in which two electrons have been removed from the cyclobutenyl radical, rather than (ii), while the name "cyclobutadiene dication" implies structure (ii), in which two electrons have been removed from cyclobutadiene. The latter name is in accord with the current practice for naming radical anions and dianions derived from conjugated cycles.



bromoketone 2-bromo-3-hydroxy-2,4-diphenylcyclobutenone (I) in 96% sulfuric acid to give stable solutions of a carbonium ion, most probably the 1,3-dihydroxy-2,4-diphenylcyclobutadiene dication (II),⁵ as demonstrated by n.m.r. spectroscopy.



- I, R = C₆H₅; R' = H; X = Br
 III, R = C₆H₅; R' = C₆H₅CH₂CO, X = H
 IV, R = C₆H₅; R' = X = H
 V, R = C₆H₅; R' = H; X = OH
 VII, R = CH₃; R' = H; X = Br

Bromoketone I, m.p. 175-177^o [*Anal.* Calcd. for C₁₆H₁₁BrO₂: C, 60.95; H, 3.49; Br, 25.39. Found: C, 61.01; H, 3.67; Br, 25.23; infrared $\lambda_{\text{max}}^{\text{Nujol}}$ 5.71 μ ; ultraviolet $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$ 262 m μ , ϵ 2.29 $\times 10^4$. Methyl ether from I and diazomethane, m.p. 115-116^o. *Anal.* Calcd. for C₁₇H₁₃O₂Br: C, 62.06; H, 3.95; Br, 24.32. Found: C, 62.24; H, 4.24; Br, 24.10; $\lambda_{\text{max}}^{\text{Nujol}}$ 5.67-6.15 μ (*cf.* ref. 6a).] was obtained by the following sequence of reactions. Phenylacetyl chloride in boiling ether was treated dropwise with triethylamine to give a 67% yield of 2,4-diphenyl-3-phenylacetoxycyclobutenone (III), m.p. 120-122^o, $\lambda_{\text{max}}^{\text{Nujol}}$ 5.60, 5.70 μ , according to the procedure described by Johnson and Marshall.^{6b} Hydrolysis with sodium hydroxide in aqueous methanol gave 2,4-diphenyl-3-hydroxycyclobutenone (IV), m.p. 155-157^o (*lit.*⁷ 160^o). The methyl ether from (IV) and diazomethane had m.p. 134-135^o. *Anal.* Calcd. for C₁₇H₁₄O₂: C, 81.60; H, 5.60. Found: C, 81.86; H, 5.88; infrared $\lambda_{\text{max}}^{\text{Nujol}}$ 5.71, 6.12 μ . Bromination of IV or III with bromine in chloroform afforded I in 96% and 84% yields, respectively.

The α -bromoketone I gave an immediate precipitate with silver perchlorate in ethanol or dry acetonitrile. It dissolved in aqueous sodium bicarbonate with the formation of a transient pink color. Acidification of the cold bicarbonate solution immediately after dissolution afforded the unstable hydroxyketone, 2,3-dihydroxy-2,4-diphenylcyclobutenone (V), m.p. 188-190^o. *Anal.* Calcd. for C₁₆H₁₂O₃: C, 76.18; H, 4.80. Found: C, 76.19; H, 4.63; $\lambda_{\text{max}}^{\text{Nujol}}$ 3.0, 5.82 μ . V regenerated bromoketone I upon treatment with anhydrous hydrogen bromide in dry ether.

Bromoketone I dissolved in 96% sulfuric acid to give a deep red solution, λ_{max} 487 m μ , ϵ 1.44 $\times 10^5$. When diluted with ice-water this solution gave a precipitate of the hydroxy ketone V in near quantitative yield. The n.m.r. spectrum of the sulfuric acid solution is reproduced in Fig. 1. A comparison with that of diphenylcyclopropenium hexafluorophosphate⁸ in the same solvent and that of benzhydrol in a 1:1 mixture of thionyl chloride and 15% fuming sulfuric acid⁹ (see

(2) T. J. Katz, J. R. Hall, and W. C. Neikam, *J. Am. Chem. Soc.*, **84**, 3199 (1962).

(3) H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962).

(4) H. Hart and R. W. Fish, *ibid.*, **82**, 5419 (1960).

(5) The extent of protonation of the oxygen atoms is in no way established in the present investigation. It seems reasonable that both will be protonated in the strongly acidic medium.

(6) (a) H. H. Wasserman and E. V. Dehmow, *J. Am. Chem. Soc.*, **84**, 3786 (1962); (b) T. B. Marshall, Ph.D. Thesis, Cornell University, 1950.

(7) H. Staudinger and S. Bereza, *Ber.*, **44**, 533 (1911).

(8) (a) D. G. Farnum and M. Burr, *J. Am. Chem. Soc.*, **82**, 2651 (1960), and unpublished results; (b) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961).

(9) The n.m.r. spectrum of the deep yellow-orange solutions of benzhydrol (10%) in 1:1 thionyl chloride and 15% fuming sulfuric acid was unchanged over several hours at about 10^o. Benzhydrol could be recovered in 60% yield by dropwise addition of the aged solution to excess ice-cold aqueous sodium hydroxide with vigorous stirring.