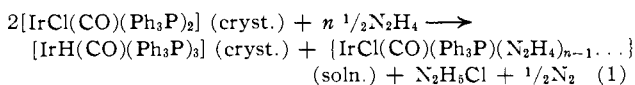


COMMUNICATIONS TO THE EDITOR

Five-Coordinate Hydrido-Carbonyl Complexes of Rhodium and Iridium and their Analogy with CoH(CO)₄
Sir:

We have synthesized quinquivalent compounds of rhodium and iridium, [MH(CO)(Ph₃P)₃], by a peculiar reaction (eq. 1) which testifies to the unique tendency of certain d⁸-complexes to five-coordination.¹ The new hydride complexes² are analogous with the carbonyl hydride of cobalt, CoH(CO)₄ (see Table I), but thermal- and air-stable, and thus amenable to detailed investigation of their structures³ and other properties.



Yellow crystals of the iridium compound are obtained by treating an ethanolic suspension of the *trans*-square complex, [IrCl(CO)(Ph₃P)₂],⁴ with an excess of hydrazine (95% aqueous solution). *Anal.* Calcd. for IrP₃C₅₅H₄₆O: Ir, 19.1; P, 9.2; C, 65.5; H, 4.6; O, 1.6. Found: Ir, 19.3; P, 9.3; C, 65.5; H, 4.5; O, 1.5. The yellow rhodium analog is synthesized from [RhCl(CO)(Ph₃P)₂]⁵ by the same procedure. *Anal.* Calcd. for RhP₃C₅₅H₄₆O: Rh, 11.2; P, 10.1; C, 71.9; H, 5.1; O, 1.7. Found: Rh, 11.1; P, 10.0; C, 71.9; H, 5.3; O, 1.7. The complexes are diamagnetic, non-conducting in acetone and nitrobenzene, and the iridium compound is monomeric in benzene (mol. wt. 1008, calcd.; 990, found).⁶ These properties, together with infrared and proton resonance spectra (Table I), have led us to formulate the compounds as molecular hydride complexes of five-coordinate and univalent metals.

The method of reduction with hydrazine was first used by Malatesta⁷ to prepare zerovalent complexes of platinum, and later by Chatt and Shaw,⁸ who found that *cis*-[PtCl₂(Et₃P)₂] (but not the *trans* isomer) reacts with hydrazine to give a complex hydride, [PtHCl(Et₃P)₂] (90%). Our original objective was to apply the same procedure for synthesis of an (as yet unknown) isoelectronic (d⁸) hydride complex, [IrH(CO)(Ph₃P)₂]. The surprising result that *five*-coordinate complexes⁹ were obtained instead poses interesting mechanistic questions.

We have not yet isolated the alcohol-soluble iridium complex (formulated as a monophosphine-hydrazine compound in eq. 1), but the following evidence indicates the stoichiometry for Ir and Ph₃P given in eq. 1: the yields of the alcohol-insoluble [IrH(CO)(Ph₃P)₃] from numerous experiments have approached but never exceeded the calculated values (for eq. 1), 50% based on Ir (found, 45–50%), and 75% based on Ph₃P (found, 70–75%). When triphenylphosphine, 2–6 moles per [IrCl(CO)(Ph₃P)₂], is added initially to the reaction

mixture (eq. 1), the yield of [IrH(CO)(Ph₃P)₃] is nearly quantitative (95% based on Ir), thus representing the recommended procedure for synthesis. On the other hand, treatment of the alcohol-soluble portion (containing excess hydrazine) with Ph₃P after the reaction (eq. 1) is complete does not produce additional hydride complex, suggesting that the presence of [IrCl(CO)(Ph₃P)₂] is required during the formation of [IrH(CO)(Ph₃P)₃].

Infrared and proton resonance spectra of the rhodium and iridium complexes are given in Table I, together

TABLE I

Compound (P = Ph ₃ P)	Infrared spectrum, cm. ⁻¹ ^a			N.m.r., ^b τ(M-H)
	ν _{CO}	ν _{MH}	δ _{MH}	
CoH(CO) ₄	2043 ^c	1934 ^d	703 ^d	20.7 ^e
RhH(CO)P ₃	1926	2004	784	19.9
IrH(CO)P ₃	1930	2068	822	21.2

^a The spectra of the Rh and Ir compounds were obtained on a Beckman IR-9 high resolution spectrometer. ν_{CO} (vs) and ν_{MH} (s) were measured in C₆H₆ solution, δ_{MH} (m) in Nujol mull. ^b The spectra of the Rh and Ir hydrides were measured in CHCl₃ solution on a Varian Associates HR-60 spectrometer. ^c In vapor phase, ref. 10; only the strongest band listed (for comparison). ^d In vapor phase, data from ref. 11. ^e Ref. 12, measured in liquid and solid phase.

with those of CoH(CO)₄ reported previously.^{10–12} Comparison of metal-hydrogen vibrational spectra of the three compounds indicates an increase in frequencies on descending the group, and this sequence has been observed previously in other vertical triads of group VIII hydride complexes absorbing in the same spectral regions.¹³ The resonance of the hydridic proton of the iridium compound shows a quartet structure (*J* = 42 c.p.s.)¹⁴ with intensity ratios 1:3:3:1 of the four equally spaced bands, which indicates an interaction with phosphorus-31 nuclei (spin 1/2) and equivalence of the three coordinated phosphines. Accordingly, a trigonal bipyramidal structure is implied, and this has been confirmed by crystal structure analysis for the rhodium complex.³ Based on their X-ray powder patterns, the Rh and Ir compounds are isostructural.

Chemical and spectroscopic investigations on transition metal hydride complexes in this laboratory¹⁵ and elsewhere,^{13, 16} and crystal structure studies on these species^{17, 18} have strongly implied a covalent metal-hydrogen bond and a normal stereochemical position for hydrogen in tertiary phosphine-stabilized complexes. This view has now been substantiated by the first direct determination of a metal-hydrogen distance in a molecular complex, [RhH(CO)(Ph₃P)₃].³ Examination of the data in Table I suggests essentially the same immediate electronic environment for hydrogen and

(10) W. F. Edgell, C. Magee, and G. Gallup, *J. Am. Chem. Soc.*, **78**, 4185 (1956).

(11) W. F. Edgell and R. Summitt, *ibid.*, **83**, 1772 (1961).

(12) R. A. Friedel, I. Wender, S. L. Shufler, and H. W. Sternberg, *ibid.*, **77**, 3951 (1955).

(13) For references, see J. Chatt, *Proc. Chem. Soc.*, 318 (1962).

(14) The spectrum of [RhH(CO)(Ph₃P)₃] shows a broad band which could not be resolved. In this case a further splitting by Rh¹⁰¹ would be expected (cf. ref. 13).

(15) L. Vaska, *J. Am. Chem. Soc.*, **83**, 756 (1961); L. Vaska and J. W. DiLuzio, *ibid.*, **83**, 1262, 2784 (1961); *ibid.*, **84**, 679, 4989 (1962); and unpublished results.

(16) L. Malatesta, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 475.

(17) P. H. Owston, J. M. Partridge, and J. M. Rowe, *Acta Cryst.*, **13**, 246 (1960).

(18) P. L. Orioli and L. Vaska, *Proc. Chem. Soc.*, 333 (1962).

(1) R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961).

(2) [IrH(CO)(Ph₃P)₃] has been synthesized also by L. Malatesta (by a different method), Symposium "Current Trends in Organometallic Chemistry," Cincinnati, Ohio, June 12–15, 1963.

(3) S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3501 (1963).

(4) L. Vaska and J. W. DiLuzio, *ibid.*, **83**, 2784 (1961).

(5) Prepared by the same method as [IrCl(CO)(Ph₃P)₂], see ref. 4.

(6) [RhH(CO)(Ph₃P)₃] is highly dissociated in benzene solution (mol. wt. 919, calcd.; 407, found).

(7) L. Malatesta and R. Ugo, *J. Chem. Soc.*, 2080 (1963), and references quoted.

(8) J. Chatt and B. L. Shaw, *ibid.*, 5075 (1962), and references cited therein.

(9) The following discussion is equally applicable to the preparation of [RhH(CO)(Ph₃P)₃].

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 $\text{CoH}(\text{CO})_3$ 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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RECEIVED AUGUST 30, 1963

Studies of the Metal-Hydrogen Bond: Structure of $\text{HRh}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_3$ ¹

Sir:

We wish to report the determination of the structure, including the Rh-H bond length, of $\text{HRh}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_3$ (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 $\text{HCo}(\text{CO})_4$, 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 $\text{HCo}(\text{CO})_4$. 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 $1.72 \pm 0.15 \text{ \AA}$, 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 ($< 1.2 \text{ \AA}$) 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 - $P2_1/n$, with four molecules in a cell of dimensions $a = 10.11 \pm 0.05$, b (unique axis) $= 33.31 \pm 0.15$, $c = 13.33 \pm 0.07 \text{ \AA}$, $\beta = 90.0 \pm 0.1^\circ$ ($\rho_c = 1.36$, $\rho_0 = 1.33 \text{ g./cm.}^3$). No symmetry conditions are imposed on the molecule. Multiple-film integrated Weissenberg data collected at room temperature with Cu $K\alpha$ 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 (s from a broad-line n.m.r. study of $\text{H}_2\text{Fe}(\text{CO})_5$ ²⁰ where, on the assumption of a pure sample and the absence of intermolecular effects, the H-H distance is found to be $1.88 \pm 0.05 \text{ \AA}$. 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 $(\text{C}_6\text{H}_5)_2\text{MoH}_2$ to be $1.1 \pm 0.2 \text{ \AA}$.

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

(6) It has already been shown that for $\text{HCo}(\text{CO})_4$ ² 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.

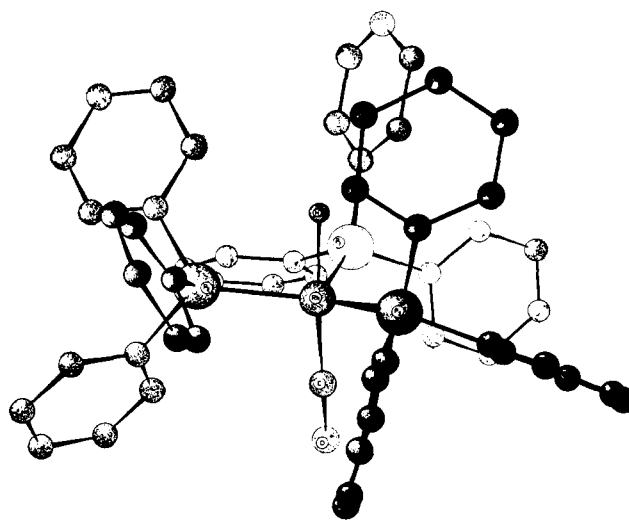


Fig. 1.—A perspective drawing of one molecule of $\text{HRh}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_3$ as viewed from 40° .

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/\AA^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 ($\mu_{\text{Cu}} = 34 \text{ cm.}^{-1}$) and because problems with white radiation are not serious with Cu $K\alpha$; (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 $t_0 = 0.416 \text{ \AA}^{-1}$, 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 \AA , and average 1.830(22) \AA . 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 \AA . from the least-squares calculations.