Infrared Spectra and Structures of Hydridocarbonyl Complexes of Transition Metals

Sir:

A resonance interaction between the vibrational states of metal–hydrogen (ν_{MH}) and carbonyl (ν_{CO}) stretching motions in certain hydridocarbonyl complexes of iridium, rhodium, and osmium offers itself as a powerful aid in deducing the molecular structures of these and analogous compounds. In favorable cases, a complete coordinational configuration of the central atom can be determined.

The interaction occurs when the hydrogen and carbonyl ligands are *trans* to one another (Figure 1, Iβ,

No.	Molecular Configuration	Hydride		Deuteride		
		ν_{MH}	ν_{CO}	ν_{CO}	ν_{MD}	ν_{MH}/ν_{MD}
I	OC, Ir, Cl, H,Dα, H,Dβ, P	2196 (α) / 2100 (β)	1982 →	2003	1575 (α) / 1497 (β)	1.394 (α) / 1.403 (β)
II	OC, Ir, Cl, Cl, H,D, P	2240	2027 =	2027	1608	1.393
III	OC, Os, P, H,Dα, H,Dβ, P	2051 (α) / 1852 (β)	1950 ←	1918	1470 (α) / 1350 (β)	1.397 (α) / 1.372 (β)
IV	OC, Os, P, H,D, Cl, P	2097	1912 =	1912	1506	1.392
V	H,D, P, Ir, P, C, O	2123	1921 →	1939		
VI	H,D, P, Rh, P, C, O	2041	1923 →	1954		

Figure 1. Diagrams of molecular structures of hydrido- and deuteriocarbonyl complexes of iridium, osmium, and rhodium; P = Ph₃P. Heavy lines refer to the H,D–CO *trans* relationship. Metal–hydrogen (ν_{MH}), metal–deuterium (ν_{MD}), and carbonyl (ν_{CO}) stretching frequencies from the infrared spectra of the crystalline complexes measured as Nujol and halocarbon mulls. The isotopic factors are ratios of the observed frequencies.

IIIβ, V, VI);[1] it is not observed when the two ligands occupy *cis* positions (Figure 1, Iα, II, IIIα, IV).[1] The presence or absence of the interaction is revealed by comparing the pertinent infrared spectral data of the hydrido and deuterio forms of the same complex (see Figure 1). The resonance manifests itself through a ν_{CO} shift and an anomalous ν_{MH}/ν_{MD} ratio (Iβ, IIIβ),[1] and these observations are readily interpretable as result-

(1) Roman numerals refer to the complexes shown in Figure 1; α and β indicate two different hydrogens or deuteriums in I and III.

ing from a repulsion of the ν_{MH} and ν_{CO} vibrational levels.[2]

The phenomenon is illustrated by the six pairs of hydridodeuteriomonocarbonyl complexes shown in Figure 1. The molecular configurations of the hydrides have been determined as quoted below. Each hydride is isostructural with the corresponding deuteride.[3] Comments on the individual complexes and the interpretation of their infrared spectral data follow.

I [(H₂,D₂)IrCl(CO)(Ph₃P)₂] have been reported previously.[5,6] The dideuteride is unique in that it can be prepared easily in high isotopic purity (>99%).[5,7] As a consequence, the dihydride emerged as the first hydridocarbonyl complex in which the ν_{MH}–ν_{CO} coupling became clearly evident,[8] and it thus led to the examination of the effect in other complexes.

Assuming that the ν_{CO} shift in the spectra of I (Figure 1), 21 cm⁻¹, represents the interaction energy (E_i) of the two vibrational states, $\nu_{IrH(\beta)}$ and ν_{CO}, we can calculate the energy of the "unperturbed" state $\nu_{IrH(\beta)}$ (*i.e.*, in the *absence* of interaction).[9] This value, 2079 cm⁻¹,[9] yields a new H–D isotopic factor, $\nu_{IrH(\beta)}$(calcd)/$\nu_{IrD(\beta)}$(obsd) = 1.389, which is in the range of the H–D factors observed for noninteracting M–H vibrational states (Iα, II, IIIα, IV).[10]

II [Ir(H,D)Cl₂(CO)(Ph₃P)₂].[11] The deuteride was prepared in high isotopic purity (99%) by treating the *crystals* of [IrCl(CO)(Ph₃P)₂][11] with dry DCl gas. The composition and structure[12] of this complex differ from I only in one respect: the "resonating" H_β in I has been replaced by Cl.[5] The spectral data of this compound demonstrate the absence of interaction between H and CO in *cis* positions: the ν_{CO} remains unshifted in the deuteride, and the value of the isotopic factor is normal. Thus, these observations corroborate the interpretation of the interaction in I.

III [Os(H₂,D₂)(CO)(Ph₃P)₃]. The dihydride was prepared by refluxing a suspension of [OsHCl(CO)(Ph₃P)₃][13] in a solution of sodium hydroxide in 2-meth-

(2) See, for example (a) G. W. King, "Spectroscopy and Molecular Structure," Holt, Rinehart and Winston, Inc., New York, N. Y., 1964, pp 348–350; (b) F. A. Cotton, "Chemical Applications of Group Theory," John Wiley and Sons, Inc., New York, N. Y., 1963, p 266.

(3) This has been established by examining the X-ray diffraction patterns of the crystalline complexes. The configurational identity of the isotopic pairs of complexes, which is the basis for the comparative analysis of the infrared spectral data, cannot be assumed without proof. We have encountered at least one hydride complex which, on deuteration, undergoes isomerization.[4]

(4) L. Vaska, forthcoming publications.

(5) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 679 (1962).

(6) L. Vaska and R. E. Rhodes, *ibid.*, **87**, 4970 (1965).

(7) This condition greatly facilitates the detection of the presence or absence of the resonance interaction since the $\Delta\nu_{CO}$ is usually not large (Figure 1).

(8) At the time the original note on I was published,[5] the structure of the complex had not been established conclusively, and only one ν_{IrD} was observed.[5] Accordingly, the meaning of the "isotope effect" (ν_{CO} shift)[5] was not appreciated. Subsequently, the molecular configuration of I was determined by nmr measurements,[4,6] and the second Ir–D stretching band (β, Figure 1) was found through a detailed examination of high-resolution infrared spectra. The frequencies for I in Figure 1 are more accurate than those reported in the original note.[5]

(9) $2100 (\nu_{IrH(\beta)}) - 21 (E_i) = 2079$ cm⁻¹ = $\nu_{IrH(\beta)}$(calcd).[2b]

(10) Analogous data are obtained for the bromo and iodo derivatives of I, *i.e.*, $\nu_{IrH(\beta)}/\nu_{IrD(\beta)} > \nu_{IrH(\alpha)}/\nu_{IrD(\alpha)} \cong \nu_{IrH(\beta)}$(calcd)/$\nu_{IrD(\beta)}$.

(11) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961). The spectral data in Figure 1 are more accurate than those previously reported.[11]

(12) The configuration of this complex follows from a detailed analysis of the infrared spectrum between 200 and 4000 cm⁻¹.[4]

(13) L. Vaska, *J. Am. Chem. Soc.*, **86**, 1943 (1964).

oxyethanol.[14] The dideuteride was synthesized in ca. 70% isotopic purity by refluxing a suspension of the dihydride in C_2H_5OD (9 days under N_2). The resonance interaction in this complex is analogous with that in I except that $\nu_{OsH(\beta)}$ is of lower energy than ν_{CO}. Accordingly, ν_{CO} shifts to a *lower* frequency in the dideuteride, and $\nu_{OsH(\beta)}/\nu_{OsD(\beta)}$ is *smaller* than $\nu_{OsH(\alpha)}/\nu_{OsD(\alpha)}$. On removing the interaction (as shown above for I, ref 9), and using the resultant ("unperturbed") $\nu_{OsH(\beta)}$, 1884 cm^{-1}, we obtain $\nu_{OsH(\beta)}(calcd)/\nu_{OsD(\beta)}(obsd) = 1.396$, which is practically identical with the observed value of $\nu_{OsH(\alpha)}/\nu_{OsD(\alpha)}$.

The molecular configuration of this complex has been determined solely from the infrared spectral data given in Figure 1. There are three possible geometrical isomers, but the presence of the resonance is expected only in one, III.[15]

IV [Os(H,D)Cl(CO)(Ph$_3$P)$_3$]. The hydride,[13] pure deuteride,[16] and the structure[17] of the complex have been reported previously. The data are shown to substantiate[18] the interpretation of the spectra of III.

V [Ir(H,D)(CO)(Ph$_3$P)$_3$] and VI [Rh(H,D)(CO)-(Ph$_3$P)$_3$]. The hydrides[20] and their structures[20,21] have been previously described. The H–CO resonance interaction in these complexes was discovered after it became possible to prepare pure deuterides[7] by reaction with D_2.[16] The M–D stretching bands have not been definitely located because of an interfering spectral band of Ph$_3$P, the position of which suggests that $\nu_{MH}/\nu_{MD} > 1.4$.[4]

The results of the present study suggest that the vibrational interaction is likely to be present in all ternary carbonyl hydrides of transition metals,[22] e.g., FeH$_2$-(CO)$_4$[23] and CoH(CO)$_4$.[24] Because of their low thermal stability and high chemical reactivity, the spectra–structure correlations on these catalytically important compounds[25] have long been a subject of complications and an accompanying controversy.[22]

(14) The colorless dihydride has been characterized by complete elemental analysis and magnetic (diamagnetic), molecular weight (monomeric in CHCl$_3$), conductivity (nonconducting in C$_6$H$_5$NO$_2$), and dipole moment (6.80 D. in benzene) measurements.

(15) In the remaining two isomers, (i) the hydrogens are *trans* to one another, and (ii) both hydrogens are *trans* to the Ph$_3$P ligands.

(16) L. Vaska, "Proceedings of the 8th International Conference on Coordination Chemistry," V. Gutmann, Ed., Springer-Verlag, Vienna and New York, 1964, p 99.

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

(18) The bromo derivative of IV and the isostructural ruthenium compounds[19] show the same properties, *i.e.*, there is no H–CO interaction in these complexes.

(19) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 1262 (1961).

(20) S. S. Bath and L. Vaska, *ibid.*, **85**, 3500 (1963).

(21) S. J. La Placa and J. A. Ibers, *Acta Cryst.*, **18**, 511 (1965).

(22) There are two recent review articles which cover practically all the aspects of transition metal hydride complexes, including carbonyl hydrides: (a) A. P. Ginsberg in "Transition Metal Chemistry," Vol. 1, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1965, Chapter 3; this is the most comprehensive treatment of the subject to date. (b) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, **7**, 115 (1965).

(23) Isoelectronic (d^6) and probably isostructural with I and III.

(24) Isoelectronic (d^6) and probably isostructural with V and VI.[20]

(25) I. Wender, H. W. Sternberg, R. A. Friedel, S. J. Metlin, and R. E. Markby, "The Chemistry and Catalytic Properties of Cobalt and Iron Carbonyls," Bulletin 600, U. S. Bureau of Mines, U. S. Government Printing Office, Washington, D. C., 1962.

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Lithium–π-Electron Interactions in But-3-enyllithium[1]

Sir:

The structure, unique bonding, and ability of alkyllithium compounds to promote stereospecific polymerizations has caused considerable interest in these derivatives.[2] In particular, it has been shown that polymerizations of butadienes, initiated by alkyllithium compounds in polar solvents, yield polymers with a 1,4-*trans* configuration typical of anionic polymerization. However, when these same polymerizations are carried out in hydrocarbon solvents the 1,4-*cis* product is obtained in up to 95% yield.[3] It is this latter observation on which we wish to comment. The generally accepted interpretation of the kinetic data of these polymerizations in hydrocarbon solvents involves two steps: the dissociation of alkyllithium hexamer (or tetramer) into an "active monomer" (the rate-determining step), followed by addition of this moiety to the diene substrate. The stereospecificity of the reaction is said to be determined by an interaction of the lithium atom with the π electrons of the diene. The total reaction leaves a new organolithium compound which may either reassociate or undergo further reaction. It is significant that the critical step (the lithium–π-electron interaction) in the control of the stereochemistry of the reaction has never been experimentally observed.

In this paper evidence is presented for an interaction between the vacant orbitals on the hexameric lithium framework and the π orbitals on the butene moiety in but-3-enyllithium. A structure consistent with the observed nmr, ultraviolet, and infrared spectra of the hexamer and which is also consistent with all of the presently known structural details of lithium derivatives is given in Figure 1. This model also can explain the stereospecific addition in hydrocarbon solvents since the geometry of the hexameric lithium–π-complex would favor *cis* addition.

In order to prove that this interaction takes place a series of compounds of the type $H_2C=CHCH_2CH_2X$ (X = H, Cl, Br, HgCl, HgR, and Li) were prepared and their nmr spectra obtained (Table I). An examination of these data shows a regular variation of the chemical shift with the electronegativity of the substituent. The one exception to this trend is the lithium derivative. In this case, the protons are less shielded than expected, with the greatest discrepancy occurring for the vinyl

(1) Taken in part from the Ph.D. dissertation of James B. Smart, Wayne State University, 1966.

(2) T. L. Brown, *Advan. Organometal. Chem.*, **3**, 365 (1965).

(3) A. U. Tobolsky and G. E. Rogers, *J. Polymer Sci.*, **40**, 73 (1959); Yu. L. Spirin, D. K. Polyakov, A. R. Grantmakher, and S. S. Medvedev, *Dokl. Akad. Nauk SSSR*, **139**, 899 (1961).