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Activation of Covalent Molecules by Some Noble Metal Complexes: The Role of the Metal[1]

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Thermodynamic data are presented and compared for the reversible addition of some small molecules to isostructural d^8 complexes of rhodium and iridium. The results, together with related observations on other noble metal complexes, are assessed in terms of the role of the metal in these interactions which are interpreted as generalized acid-base reactions. The sequences of stability (K_C) and heats of formation ($-\Delta H^O$) of metal complex adducts with acid molecules (H_2, O_2, SO_2) are, or appear to be: third row metal > second row metal ($Ir > Rh$). With «amphoteric» molecules (CO, C_2H_2, C_2H_4), the role of the metal emerges as a more complex one, and the limited thermodynamic data presently available allow no clear definition of the factors which determine the activation of these species.

Introduction

Platinum and its congeners in group VIII have performed an historic function in the development of catalysis, and their importance in this field continues unabated. This statement embraces also a relatively recent branch of catalytic science: homogeneous catalysis by metal complexes in solution. A special significance of the latter discipline has been emerging from its ability to enlighten our understanding of the principles underlying catalytic reactions at large, an ability not very deeply engraved in surface catalysis.

Numerous discussions on the factors which influence the catalytic activation of small molecules by metal complexes have been printed in recent years[2-11] (just to cite some selected articles on the subject). These expositions testify to the progress in the rapidly developing field, but they also demonstrate a scarcity of quantitative dynamic data on these reactions, so that much of the discussion of mechanisms and controlling factors has been resting on qualitative or indirect evidence.

Our efforts have been focusing on attempts to separate and define the roles of the individual reactants through (i) a quantitative comparison of a group of closely related reactions,[12] and (ii) a subsequent comparison of several different groups of such reactions.[11] In a previous article[11] we examined the role of some covalent molecules (XY) in their activation by a metal complex, and concluded that these reactions (equation 1) can best

$$[IrCl(CO)(Ph_3P)_2]+XY \rightleftarrows [(XY)IrCl(CO)(Ph_3P)_2] \tag{1}$$

$XY = H_2, O_2, SO_2, CO, C_2H_4$, cyano-ethylene, hydrogen halide, halogen etc.

be interpreted as acid-base interactions, that is, the stability of the adduct, K_C (equation 2), was found to be proportional to an electron-accepting property of XY.[11] These conclusions have since been substantiated by a related study.[13]

Another aspect of these inquiries is the problem of defining the role of the metal complex. This subject may be divided into the functions of (i) the metal and (ii) the ligands. Each of these functions is subject to further analysis. The ligands regulate the activity of the complex through their electronic as well as steric properties.[12] The role of the metal may be analyzed in terms of its position in the periodic table, its formal oxidation state and non-bonding electronic configuration, and the various consequences of these properties, such as stereochemistry (coordination number and symmetry) and basic or acid behavior toward the covalent molecule. In this paper we confine our remarks to some of our recent observations on the latter subject, in particular, the «role of the platinum group metal».[1]

It should immediately be recalled that in a chemical reaction the functions of all participants are inter-

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(1) Based on a lecture given at the Symposium on Platinum Group Metals, 158th National Meeting of the American Chemical Society, New York, N.Y., September 7-12, 1969. The paper represents a summary of the researches carried out in the author's laboratory on the subject given in the title.

(2) G.C. Bond, in «The Role of the Adsorbed State in Heterogeneous Catalysis», *Disc. Faraday Soc. No. 41*, The Faraday Society, London, 1968, p. 200

(3) (a) J.P. Collman, *Transition Metal Chem.*, *2*, 1 (1966); (b) *Accounts Chem. Res.*, *1*, 136 (1968); (c) J.P. Collman and W.R. Roper, *Advan. Organometal. Chem.*, *7*, 53 (1968).

(4) R. Cramer, *Accounts Chem. Res.*, *1*, 186 (1968).

(5) (a) J. Halpern, in «Proceedings of the Third International Congress on Catalysis», W.M.H. Sachtler *et al.*, eds., North-Holland Publishing Co., Amsterdam, 1965, Vol. 1, p. 146; (b) in « Homogeneous Catalysis», *Advances in Chemistry Series No. 70*, R.F. Gould, ed., American Chemical Society, Washington, D.C., 1968, p. 1; (c) in «Homogeneous Catalysis with Special Reference to Hydrogenation and Oxidation», *Disc. Faraday Soc. No. 46*, The Faraday Society, London, 1968, p. 7.

(6) R.F. Heck, *Accounts Chem. Res.*, *2*, 10 (1969).

(7) J.A McGinnety, N.C. Payne, and J.A. Ibers, *J. Am. Chem. Soc.*, *91*, 6301 (1969).

(8) R. Nyholm, in « Proceedings of the Third International Congress on Catalysis», W.M.H. Sachtler *et al.*, eds., North Holland Publishing Co., Amsterdam, 1965, Vol. 1, p. 25.

(9) W. Strohmeier, *Structure and Bonding*, *5*, 96 (1968).

(10) (a) R. Ugo, *Coordin. Chem. Rev.*, *3*, 319 (1968); (b) *Chimica Industria*, *51*, 1319 (1969); (c) S. Carra' and R. Ugo, *Inorg. Chim. Acta Rev.*, *1*, 49 (1967).

(11) L. Vaska, *Accounts Chem. Res.*, *1*, 335 (1968), and references quoted in this article.

(12) L. Vaska and M.F. Werneke, *Trans. New York Academy Sciences*, in press.

(13) A.J. Deeming and B.L. Shaw, *J. Chem. Soc. A.*, 1802 (1969).

Table I. Comparison of Rhodium and Iridium: Thermodynamic and Infrared Spectral Data for the Reactions with Sulfur Dioxide

$trans\text{–}[MCl(CO)(Ph_3P)_2] + SO_2 \leftrightarrows trans\text{–}[SO_2)MCl(CO)(Ph_3P)_2]$

M	ΔF° kcal mole^{-1}	ΔS° e.u.	ΔH° kcal mole^{-1}	Infrared Data, cm^{-1} $\nu_{M\text{-}S}$ [b]	$\Delta\nu_{SO_2}$ [c]	$\Delta\nu_{CO}$ [d]
Rh	−2.6	−17	−7.9	295	−87	+51
Ir	−4.3	−21	−10.5	315	−95	+56

[a] In Chlorobenzene, 30°C. The thermodynamic parameters have been calculated from equilibrium constant data (cf. equation 2) 10-60°C, obtained by a spectrophotometric method. [b] Metal-sulfur stretching frequency (in crystals). [c] $\Delta\nu_{SO_2} = \nu_1$ for SO_2 in complex minus ν_1 for free SO_2 (both in chloroform solution). [d] $\Delta\nu_{CO} = \nu_{CO}$ in $[(SO_2)MCl(CO)(Ph_3P)_2]$ minus ν_{CO} in $[MCl(CO)(Ph_3P)_2]$ (both in $CHCl_3$).

dependent, and thus, the role of the metal cannot be separated, first of all, from that of the metal complex, and further, from the other components of the reaction such as the reaction partner (XY), and the environment (solvent). Although this observation poses a definite limitation for any assessment of this type, it is possible to separate the various factors and roles phenomenologically, the significance of which will depend on the availability and selection of the reactions to be analyzed.

The discussion given below is based on data derived from thermodynamic and kinetic studies on the reactions typified in equation 2, and from spectral and structural properties of the participating complexes.

$$ML_i + XY \underset{k_{-1}}{\overset{k_2}{\leftrightarrows}} (XY)ML_i \tag{2}$$

M = central metal atom; L_i = ligands

XY = HCl, H_2, O_2, SO_2, CO, C_2H_2, C_2H_4, etc.

$K_c = [(XY)ML_i]/[ML_i][XY] = k_2/k_{-1}$

Vertical Comparisons

In order to evaluate the role of the metal, it is necessary to compare formally isostructural and isoelectronic complexes, that is, those which differ only in the metal. In principle, this is possible with the metals situated in the same vertical group or triad. In practice, it seems that only some pairs of d^8 complexes of rodium and iridium have been subject to a *quantitative* comparison as activators of covalent molecules according to equation 2.

In view of the widely different electronic and structural properties of the molecules (XY, equation 2) which have been found to react reversibly with metal complexes, one would anticipate that the role of the metal may not be entirely independent of the nature of XY — as we would expect,[11] and indeed find, that the behavior of the various covalent molecules depends on the type of activator complex. For example, the sequence of stability (K_C, equation 2) of the hydrogen and oxygen adducts of $[IrCl(CO)(Ph_2P)_3]$ (d^8) is different from that of the same adducts of $Pt(Ph_3P)_2$ (d^{10}): for Ir^I, $H_2 > O_2$[11,14] but for Pt^0, $O_2 \gg H_2$[15] (addition of H_2 to $Pt(Ph_3P)_n$ is not observable under normal conditions[15] and the effect does not appear to be a kinetic one[16]).

Reactions with Acid Molecules. Table I gives an example of our data on the reactions of pairs of four-coordinated d^8 complexes of univalent Ir and Rh with «acid» addenda (XY).[17,18] By «acid» we refer to molecules which act as electron acceptors or oxidants with respect to the particular complex under observation, that is, we do not preclude the possibility of the same «acid» behaving as a base or reductant toward some other complex. Such a characterization of a molecule and its reactions requires, of course, an experimentally observable indicator. This is available for the model compounds discussed in this paper: the sign and magnitude of the $\Delta\nu_{CO}$ (Table I) are indicative of the direction and extent, respectively, of the «net electron transfer» between the metal and the addendum.[11] According to an interpretation discussed previously,[11] the activator complexes in Table I act as bases (donors, reductants) and sulfur dioxide as an acid (acceptor, oxidant) in these reactions ($\Delta\nu_{CO}$ is positive). Numerous other molecules (XY) have been found to exhibit similar (acid) behavior in their reactions with *trans*–$[MA(CO)L_2]$ (A = univalent anionic ligand; L = monodentate neutral ligand).[11] For the activation of SO_2, there is an additional indicator which corroborates with the interpretation of the ν_{CO} shift: the decrease in the S–O stretching frequencies (Table I) testifies to a reduced state of sulfur dioxide in the adducts.

Our next question concerns the relative base strength of the two activator complexes. If the ν_{CO} in $[MCl(CO)(Ph_3P)_2]$ is taken as a label for «latent or static basicity», the iridium complex emerges as a stronger base (ν_{CO} (cm^{-1}) in $CHCl_3$: Ir, 1965; Rh, 1983). We further note that the difference between the «inherent basicities» (ν_{CO}) of the two complexes is manifested also in their reactions with sulfur dioxide. According to the spectral shifts, $\Delta\nu_{CO}$ and $\Delta\nu_{SO_2}$, both of which are larger for the iridium pair (Table I), the extent of oxidation of the Ir^I complex is somewhat greater than that of the Rh^I analog. These observations are in agreement with the commonly suggested order of the electronic promotion energies (E_p) for the third and second row transition metals,[8,10] *i.e.*, E_p: Ir < Rh.

Thermodynamic data in Table I demonstrate a clear difference in stability of the two SO_2 adducts, and conform with the above interpretation of the spectra that the basicity sequence of the activator complexes is Ir > Rh. Since the reactant as well as the product complexes are isostructural pairs,[19] and since the planar symmetry of the *trans*–$[MCl(CO)(Ph_3P)_2]$ remains

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(14) L. Vaska, in «Progress in Coordination Chemistry», M. Cais, ed., Elsevier, New York, N.Y., 1968, p. 13.

(15) R. Ugo, S. Pasini, S. Cenini, A. Fusi, and F Conti, in «Progress in Coordination Chemistry», M. Cais, ed., Elsevier, New York, N.Y., p. 156.

(16) L. Vaska, unpublished results.

(17) L. Vaska, in « Proceedings of the First International Symposium», U. Croatto, ed., *Inorganica Chimica Acta*, Padova, 1958, p. E1.

(18) L. Vaska and J. Peone, Jr , in preparation.

essentially unaltered in the products, *trans*–[$(SO_2)MCl(CO)(Ph_3P)_2$],[19] the difference in the enthalphy changes (ΔH^O) of the two reactions (2.6 kcal mole^{-1}) appears to reflect the difference in the metal-SO_2 bond dissociation energies (D_{M-SO_2}). The metal-sulfur stretching frequency (ν_{M-S}) also points to a significant difference between the Ir–S and Rh–S bond strengths. It is to be noted that the structural parameters of the two molecules, *trans*–[$(SO_2)MCl(CO)(Ph_3P)_2$], as determined by X-ray diffraction,[19] do not very clearly reflect these differences in the thermodynamic and spectroscopic properties. The data on the chloro complexes (Table I) represent but one example of a series of analogous results of the reactions of a number of iridium and rhodium complexes with sulfur dioxide.[17,18] In most cases the difference between the two metals is considerably larger; for example, the reactions of the iodides, [$MI(CO)(Ph_3P)_2$], with SO_2 (in C_6H_5Cl) are accompanied by the enthalpy changes (ΔH^O) of –9.4 for M = Rh and –25 kcal mole^{-1} for M = Ir.

The reactions given in Table I have a close analogy with adduct formation between sulfur dioxide and amines, for which the negative values of all three thermodynamic parameters ($-\Delta F^O$, $-\Delta S^O$, $-\Delta H^O$) increase with increasing basicity (pK_a) of the amine[20] (cf. Table I). Furthermore, the magnitudes of these energy changes are in the same range as we find for the metal-complex-SO_2 reactions[17] (Table I), *e.g.*, for some derivatives of aniline- and toluidine-SO_2 complexes, $\Delta H^O = -15$ to -25 kcal mole^{-1} have been reported.[20] Also, the sulfur-metal and sulfur-nitrogen (of the amine) bonds show a certain analogy in that they have been considered to result from an electron donation from the metal or nitrogen into an antibonding orbital of SO_2 localized mainly on the sulfur atom.[20,21] Thus, it seems that as far as the reactions with sulfur dioxide are concerned, the metal complexes under discussion are not unlike amines, or, one might say, the base strengths of these complexes are similar to those of the amines cited. In fact, we can extend this analogy to include the reactions of most of the acid molecules (as defined above, equation 2)[11] with conventional bases and metal complexes. The transition metal complexes and the metals theselves are, of course, vastly more versatile reactants than common Lewis bases, owing to a larger number and variety of valence orbitals they possess. The reactions of the iridium and rhodium complexes under consideration (Tables I, III) are also more informative (with respect to the electronic nature of the interactions) than those of conventional bases with acids. For instance, the base strength of an amine is usually defined in terms of the thermodynamic properties of its reactions (pK_a, ΔH^O), while our model compounds exhibit additional and independent information as to their relative basicity or acidity which has been found to be proportional to that in the thermodynamic scale (Table I).

The analysis of the results detailed above applies also to the reactions of these and related pairs of rhodium and iridium complexes with all of the acid molecules (*e.g.*, O_2, cyano-ethylenes, halogens, protonic acids, etc.) which we have examined.[11] The SO_2 system has been chosen as an illustration because it provides quantitative thermodynamic as well as spectral data for both complexes (some molecules (*e.g.*, H_2, O_2) show no measurable reaction with [$RhA(CO)$-$Ph_3P)_2$] under normal conditions).

A comparison of kinetic data of the reactions of an isoelectronic pair of chelated cationic complexes, [$M(P\text{–}P)_2$]Cl (M = Ir, Rh; P–P = $Ph_2PCH_2CH_2PPh_2$),[22] with molecular hydrogen and oxygen is given in Table II. The order of reactivity, Ir > Rh, is found to be the same as that of the stability of the SO_2 adducts (Table I). Structural data on the two oxygen complexes, [$O_2M(P\text{–}P)_2$]$^+$, show a marked difference between the O–O bond lengths in the two compounds, 1.63 Å (Ir) and 1.42 Å (Rh), indicating that the O_2 is more extensively reduced in the iridium than the rhodium complex.[7] It is interesting to note that the data in Table II suggest an acidity order of $H_2 > O_2$ relative to the iridium complex (which is the same as found for other Ir complexes,[11,14] while for the rhodium complex it appears to be the reverse, $O_2 > H_2$, as found also for the d^{10} zerovalent platinum complex cited above.[15]

Table II. Comparison of Iridium and Rhodium: Kinetic and Activation Data for the Reactions with Molecular Oxygen and Hydrogen [a]

$$[M(P\text{–}P)_2]Cl + XY \overset{k_2}{\rightleftarrows} [(XY)M(P\text{–}P)_2]Cl \;^{b}$$

M	XY	k_2 [c] $M^{-1}\,sec^{-1}$	ΔH^* kcal mole^{-1}	ΔS^*, e.u.
Rh	O_2	1.1	7.9	–35
Ir	O_2	3.3	3.6	–44
Rh [d]	H_2	—	—	—
Ir	H_2	910	2.4	–37

[a] In chlorobenzene, 30°C. [b] P–P = $Ph_2PCH_2CH_2PPh_2$. [c] Second-order rate constant for the addition reaction. [d] No reaction observed at 30°C and p_{H_2}, 700 mm.

No data analogous to those presented above (Tables I, II) appear to be available for isoelectronic and isostructural pairs of osmium-ruthenium and platinum-palladium complexes. Considerable amount of spectroscopic and qualitative chemical evidence speaks, however, for the same kind of relation as found for Ir and Rh, *i.e.*, K_C (equation 2), etc.: third row metal > second row metal. For example, the order of stability of the oxygen adducts of zerovalent platinum and palladium, [$O_2M(Ph_3P)_2$], is Pt > Pd,[23] and the addition of hydrogen chloride to the d^8 complexes, [$MHCl(Et_3P)_2$], has been reported to occur for M = Pt but apparently not for M = Pd.[24] Numerous similar observations can be cited, including those on pairs of Os–Ru complexes. For the chemisorption of hydrogen and oxygen, the relationship between the second and third row metal is less clear. The differences, if any, in the heats and strengths of chemisorption appear to be small, and the usual problems with heterogeneous systems make an accurate comparison difficult.[25]

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(19) (a) S.J. La Placa and J.A. Ibers, *Inorg. Chem.*, *5*, 405 (1966); (b) K.W. Muir and J.A. Ibers, *Inorg. Chem.*, *8*, 1921 (1969).

(20) W.E. Byrd, *Inorg. Chem.*, *1*, 762 (1962), and references quoted.

(21) L. Vaska and S.S Bath., *J. Am. Chem. Soc.*, *88*, 1333 (1966).

(22) L. Vaska and D.L. Catone, *J. Am. Chem. Soc.*, *88*, 5324 (1966).

(23) G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem.*, *79*, 62 (1967).

(24) (a) J. Chatt, L.A. Duncanson, and B.L. Shaw, *Chem. Ind.* (*London*), 859 (1958); (b) J. Chatt and B.L. Shaw, *J. Chem. Soc.*, 5075 (1962).

Reactions with Basic and Amphoteric Molecules. Simple addition reactions of organic bases with some molecular metal complexes, notably of vanadium(IV) and copper(II), are well known,[26] but comparisons with isoelectronic and isostructural species of other metals of the same vertical group appear to be absent.

Table III. Comparison of Rhodium and Iridium: Thermodynamic and Infrared Spectral Data for the Reactions with Carbon Monoxide, Ethylene and Acetylene [a]

$$[MI(CO)(Ph_3P)_2] + XY \leftrightarrows [(XY)MI(CO)(Ph_3P)_2]$$

M	XY	K_C, M^{-1}	ΔH°kcal mole^{-1}	$\Delta\nu_{CO}$,(cm^{-1}) [b]
Rh [c]	CO	30	–2	—
Ir [c]	CO	4,500	–1	+1 [d]
Rh	C_2H_4	(<1) [e]	—	—
Ir	C_2H_4	2.7	–12	–21
Rh	C_2H_2	(<1) [e]	—	—
Ir	C_2H_2	1.2	–9.3	–12

[a] In chlorobenzene, 20°C. See footnote *a* to Table I. [b] $\Delta\nu_{CO} = \nu_{CO}$ in $[(XY)MI(CO)(Ph_3P)_2]$ minus ν_{CO} in $[MI(CO)(Ph_3P)_2]$ (both as nujol mull). The ν_{CO} has not been detected for the Rh-XY complexes, cf. K_C. [c] Poor reproducibility; K_C and ΔH°, *ca.* ± 50%. [d] Average value of two ν 's (A_1 and B_2), ref 27. [e] No reaction observed for several hours in C_6H_6, C_6H_5Cl or $C_6H_5CH_3$ at 10-30°C under 700-800 mm of p_{XY}.

In Table III some thermodynamic and infrared data are compared for the reactions of $[MI(CO)(Ph_3P)_2]$ with carbon monoxide, ethylene and acetylene. The results are somewhat fragmentary, in part scattered (footnote *c*, Table III) and they reflect only weak interactions (small K_C's, unstable adducts) which altogether tend to reduce the value of the intended comparisons. Nevertheless, the data provide a valuable insight into the nature of the activation of these important molecules in that they point to the complexity of the problem at hand.

We first note that, according to our interpretation of the spectral shifts, $\Delta\nu_{CO}$, both ethylene and acetylene act as weak bases toward the iridium complex (cf. Table I, discussion above and ref. 11; as pointed out previously,[11] this interpretation is subject to limitations posed by symmetry changes accompanying these reactions). Recalling that with acid molecules the rhodium complexes showed weaker interactions than their iridium analogs, one would perhaps expect a reversal of this behavior in the reactions with these somewhat basic molecules, C_2H_4 and C_2H_2, which, however, is not what is observed (K_C in Table III). On the other hand, the data, or their absence in Table III for $[RhI(CO)(Ph_3P)_2]$ do not preclude the possibility of these reactions being exothermic and accompanied by relatively large negative entropy changes. A clue to such a possibility may be found in the comparison of the activation of carbon monoxide by the two complexes. The order of stability of the adducts is different from that of the enthalpy change: K_C (30°), Ir>Rh, but $-\Delta H^0$, Rh>Ir. Also, similar reverse sequences have been found for the reactions of CO with different halide (A) complexes, $[MA(CO)(Ph_3P)_2]$; for both M = Ir or Rh: K_C (30°), I>Br>Cl, but $-\Delta H^0$, Cl>Br>I; that is, the variance in these orders reflects relatively large differences in the entropy changes. It should be now added that the bromo and chloro derivatives of $[IrA(CO)(Ph_3P)_2]$ do not show a measurable reaction with either ethylene or acetylene (under normal conditions, footnote *e* to Table III). Thus, the behavior of these molecules seems to be at least partly analogous to that of carbon monoxide.

According to the $\Delta\nu_{CO}$ (Table III) for the reaction of $[IrA(CO)(Ph_3P)_2]$ (A = I) with carbon monoxide, there is essentially no resultant «*net* electron transfer»[11] between the parent compound and CO. For A = Cl, a shift ($\Delta\nu_{CO}$) of –6 cm^{-1} has been reported.[11,27] Thus, carbon monoxide apears to act as a neutral or slightly basic molecule with respect to these particular iridium complexes. The basicity sequence ($\Delta\nu_{CO}$) for the three unsaturated molecules (as derived from their reactions with $[IrI(CO)(Ph_3P)_2]$) is: $C_2H_4 > C_2H_2 >$ CO, which is the same as that of the $-\Delta H^0$'s for their reversible activation, and the latter is similar to the reported order of heats of chemisorption of these molecules on metal surfaces, $C_2H_2 \sim C_2H_4 >$ CO (for any metal).[25] This relative agreement is perhaps somewhat unexpected since the adsorption of C_2H_4 and C_2H_2 on metals includes dissociation of these molecules which is not observed in the reactions cited in Table III. We have, however, found that following a *fast reversible* uptake of acetylene by $[IrI(CO)(Ph_3P)_2]$, there is a subsequent slow reaction which yields a stable hydrido-acetylide addition product, $[(C_2H)(H)IrI(CO)(Ph_3P)_2]$; the data in Table III reflect the reversible step only.

Returning to the comparison of rhodium and iridium, the stability order shown in Table III, Ir>Rh, has been found to hold also for other pairs of isostructural d^8 complexes of these metals. For example, the novel addition-substitution reactions, equation 3,[28] show, qualitatively,

$$[M(ClO_4)(CO)(Ph_3P)_2] + C_2H_4 \rightarrow [(C_2H_4)M(CO)(Ph_3P)_2]ClO_4 \qquad (3)$$

M = Rh, Ir

the same relative difference between the two metals (Ir>Rh). It seems that the stability sequence, third row metal>second row metal, is generally valid also for the other vertical pairs of group VIII metals (*i.e.*, Os>Ru, Pt>Pd) in their complexes with these and related amphoteric molecules. Spectral, kinetic and other chemical evidence has long been considered to suggest this order and the same trend is found in the recently discovered nitrogen complexes ($M-N_2$).[29] But it is certainly surprising to find that even in the case of the very widely studied olefin complexes of platinum and palladium there appear to be no strict thermodynamic comparisons available[30] (a 1969 compre-

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[25] G.C. Bond, «Catalysis by Metals», Academic Press, New York, N.Y., 1962, Chapter 5.

[26] See for example, W. Partenheimer and R.S. Drago, *Inorg. Chem.*, *9*, 47 (1970), and references quoted.

[27] L. Vaska, *Science*, *152*, 769 (1966).

[28] L. Vaska and J. Peone, Jr., submitted for publication.

[29] A.D. Allen and F. Bottomley, *Accounts Chem. Res.*, *1*, 360 (1968).

[30] F.R. Hartley, *Chem. Rev.*, *69*, 799 (1969)

hensive review on olefin and acetylene complexes of Pt and Pd citing 605 (!) references). It is noteworthy to add that for the chemisorption strength of ethylene on metal surfaces the following sequences have been suggested: Pt > Pd; Ir > Rh; Os ~ Ru.[31]

We conclude this discussion by noting (a) that the observed order of stability of the metal complex-unsaturated molecule adducts (K_C, Table III), Ir > Rh, does not seem to conform with the *simple* acid-base model applied successfully for the reactions with acid molecules, and (b) that the role of the metal in the reactions with the three amphoteric molecules (Table III) cannot be precisely defined at present, owing perhaps largely to the limited available thermodynamic data, but certainly also to our inadequate theories of the nature of the bond between a transition metal and the unsaturated molecule, *e.g.*, the σ-π dualism (cf. ref. 11).

Finally, a comment should be made on the term «amphoteric molecule» introduced here as an operational name for molecules (ligands, ions, etc.), most of which have, in recent years, acquired the designation «π-acid».[32] It seems that the latter term is misleading since it refers only to one property of what is considered to be a «dualistic» electronic system, and our data (Table III) and those of others[33] suggest that «σ-basicity» of these species (including tertiary phosphines[33]) appears to be perhaps even a more important property than the acid function. «Amphoteric» is specifically meant to refer (a) to the assumed electronic synergy of these molecules and (b) to their variable but small *net* donor-acceptor properties in metal complexes as observed experimentally (see analogous operational definition of an «acid molecule» at the outset of the preceding section).

Horizontal Comparisons

Two kinds of comparisons of metals situated in the same row of the periodic table may be considered. One of them focuses on the electronic configuration of the metal, that is, on the differences between *isovalent* species as activators for covalent molecules. This type of inquiry is the only one possible for the metals themselves, and numerous analyses and correlations of heats and strengths of chemisorption of gases on metal surfaces have been reported.[2,10,25,31] These, however, are not always subject to a straightforward interpretation because of the usual complexities associated with heterogeneous systems. For homogeneous systems of metal complexes in solution, hardly any such comparisons are available, owing largely to a lack of suitable series of isovalent complexes, but also to apparent absence of attempts to establish such correlations.

Another kind of comparison focuses on the formal oxidation state of the metal or the charge on the complex, that is, on differences between *isoelectronic* species. Although an ideal series such as (4) is

$$\underset{d^8}{Os^0L_4} \qquad \underset{d^8}{[Ir^IL_4]A} \qquad \underset{d^8}{[Pt^{II}L_4]A_2} \tag{4}$$

presently not accessible in its entirety, the data given in Table IV, albeit incomplete and mostly qualitative, demonstrate a trend which has long been predicted on general chemical evidence[3c,8,10c] but in the absence of actual comparisons involving all three platinum metals in the same period.

Table IV correlates the stability of the adducts of some four-coordinated d^8 complexes of Os^0, Ir^I, and Pt^{II} with hydrogen and hydrogen chloride with the formal oxidation state of the metal. The existence of the zerovalent osmium complex has not yet been substantiated, and the dihydrido and hydrido-chloro Os^{II} complexes, formally derived as H_2 and HCl adducts of $[Os(CO)(Ph_3P)_3]$, respectively, have been prepared by indirect methods.[35,36] Attempts to remove the «addenda» (H_2, HCl) from $[H_2Os(CO)(Ph_3P)_3]$ and $[HClOs(CO)(Ph_3P)_3]$ by subjecting their solutions to vacuum for several days have been largely unsuccessful thus far, and a prolonged treatment of the dihydride with excess deuterium at 25° has resulted only in a small fractional conversion to the dideuteride. These data testify to a very high stability of the six-coordinated osmium complexes. For the reactions of the iridium(I) complex, quantitative data are available,[11,12] and although both the H_2 and HCl adducts are isolable and stable, quantitative dissociation into reactants can be effected at ambient temperatures. The bivalent cationic complex of platinum has been reported not to combine with hydrogen or hydrogen chloride at normal conditions,[34] an observation which does not exclude the possibility of a very weak interaction (cf. Table III; except for $[IrI(CO)_2(Ph_3P)_2]$, none of the adducts given are isolable at room temperature. This result is, in fact, predictable from the very high ν_{CO} in $[PtCl(CO)(Et_3P)_2]^+$, 2110 cm^{-1}, which reflects a very low basicity or an acid-base character perhaps not very different from that of the acid reactants themselves. Similar analysis of the infrared data of the osmium complexes (Table IV) leads to the prediction for a relatively low CO stretching frequency (< 1900 cm^{-1}) in $[Os(CO)(Ph_3P)_3]$ and a corresponding instability of the complex relative to its adducts with the acid molecules. Such an auxiliary information from the ν_{CO} again illustrates a unique importance of this label in the interpretation of the results of the type of reactions under discussion.

The function of the formal oxidation state becomes evident also if one compares the activity (toward H_2) of compounds of the same metal in two different valence states: Os^0 (d^8) *vs.* Os^{II} (d^6), Ir^I (d^8) *vs.* Ir^{III} (d^6), etc., although in these instances the role of the oxidation state is intimately involved with that of the coordination number. All these comparisons appear to establish that the order of stability of the adducts, $(XY)ML_i$ (equation 2), with *acid* addenda (XY) is inversely proportional to the positive oxidation state of the metal in the activator complex, ML_i ($Os^0 > Ir^I > Pt^{II}$).

This anticipated and perhaps too obvious conclu-

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(31) G.C. Bond, in «Homogeneous Catalysis», *Advances in Chemistry Series No. 70*, R.F. Gould, ed., American Chemical Society, Washington, D.C., 1968, p. 25.

(32) F.A. Cotton and G. Wilkinson, «Advanced Inorganic Chemistry», 2nd ed., Interscience-Wiley, New York, N.Y., 1968, Ch. 27.

(33) L.M. Venanzi, *Chemistry in Britain*, *4*, 162 (1968).

(34) H.C. Clark, K.R. Dixon, and W.J. Jacobs, *J. Am. Chem. Soc.*, *90*, 2259 (1968).

(35) L. Vaska, *J. Am. Chem. Soc.*, *88*, 4100 (1966).

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

Table IV. Comparison of Some Isoelectronic Complexes of Osmium, Iridium, and Platinum. The Role of the Formal Oxidation State.

$$ML_4 + XY \leftrightarrows (XY)ML_4$$

ML_4, d^8 Complex [a]	ν_{CO} [b]	$(XY)ML_4$, d^6 Complex [a]	ν_{CO} [b]	Relative Stability [c] of $(XY)ML_4$
$([Os^0(CO)P_3])$		$[H_2Os^{II}(CO)P_3]$	1918	« Very stable »
$[Ir^ICl(CO)P_2]$	1956	$[H_2Ir^{III}Cl(CO)P_2]$	2003	« Stable »
$[Pt^{II}Cl(CO)P_2]^+$	2110	$([H_2Pt^{IV}Cl(CO)P_2]^+)$		« Unstable »
$([Os^0(CO)P_3])$		$[HClOs^{II}(CO)P_3]$	1912	« Very stable »
$[Ir^ICl(CO)P_2]$	1956	$[HClIr^{III}Cl(CO)P_2]$	2024	« Stable »
$[Pt^{II}Cl(CO)P_2]^+$	2110	$([HClPt^{IV}Cl(CO)P_2]^+)$		« Unstable »

[a] $P=(C_6H_5)_3P$; for the Pt complex(es), $P=(C_2H_5)_3P$. The formulae in parentheses represent as yet either unknown or not isolable complexes, see text. [b] C-O stretching frequency in cm^{-1}, measured in nujol. Data for $[PtCl(CO)P_2]^+$ from ref. 34; other data from ref. 35. The ν_{CO}'s given for $[H_2Os(CO)P_3]$ and $[H_2IrCl(CO)P_2]$ are those of the corresponding D_2 adducts because of a H-CO resonance interaction in the hydrides (giving a misleading ν_{CO} value); see ref. 35. [c] Refers to the equation in title; see text.

sion might be expected to show a general and universal validity, but there may be exceptions to this rule. As cited above, in contrast to the d^8 Ir^I complexes, $[IrA(CO)L_2]$, the d^{10} Pt^0 compound, $Pt(Ph_3P)_2$ (active species in solution, derived from dissociation of $Pt(Ph_3P)_4$),[10a] shows no uptake of molecular hydrogen under normal conditions;[15] yet, according to the «theory» it should exhibit a reactivity superior to Ir^I on account of three criteria usually considered to be the principal factors influencing the activity of a complex with respect to oxidative addition (Table IV): (a) oxidation state (see above), (b) d^n configuration (implying $n \propto$ basicity), and (c) coordinative unsaturation. This example thus suggests that these formal concepts (a, b, c) do not necessarily reflect a relative basicity of the complex as defined in the discussion of the data in Table I and IV. The specific behavior of $Pt(Ph_3P)_2$ appears to be rooted in both the formally closed shell electronic structure of a d^{10} configuration and the «particular acidity» of H_2 (orbital overlap criteria, etc.; see introductory discussion on the interdependence of the reactants).

No horizontal comparisons involving basic or amphoteric molecules in the reactions typified in equation 2 appear to have been reported. For the strength of ethylene chemisorption on the six platinum group metals, Bond[31] gives the following over-all order: $Pt \sim Ir > Pd > Rh > Ru \sim Os$, which, for each horizontal triad, divides into these two sequences: $Pd > Rh > Ru$, and $Pt \sim Ir > Os$.

Concluding Remark

This paper gives a brief account of our studies pertaining to the problem stated in the title, and attempts to interpret the results in terms of a simple model. One of the objectives of these inquiries has been to define the problem and analyze the various factors which must be considered for a meaningful comparison. As it happens not infrequently in such cases, the conclusions become perhaps less definite than anticipated at the outset. Although some of the quantitative data summarized here (reactions with acid molecules) simply confirm what has long been surmised on qualitative evidence, other results (reactions with basic and amphoteric molecules) point to the role of the metal as a more complex and less understood item than has generally been assumed in recent discussions of the subject.

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