Transition Metal Basicity

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The chemists' concept of *acid* and *base* has changed greatly since Arrhenius's original definition of an acid as a substance which would dissociate in water to give a hydrogen ion, and a base, to give a hydroxide ion. Brønsted, and independently Lowry, redefined the terms so as to extend their usefulness to nonaqueous solutions. This they accomplished by designating as acid any substance which donates a proton and as base any substance which accepts a proton. Lewis further generalized the terms, defining acids as species which act as electron-pair acceptors in chemical reactions, and, conversely, bases as electron-pair donors. In modern usage the electron pair often is not emphasized, so a base is simply an electron donor while an acid is an electron acceptor. It is primarily in this latter sense that we shall use the terms base and acid.

The idea of metal basicity may seem strange, because metal cations are customarily regarded as acids. However, as described in this Account, there are many complexes of metals in low oxidation states where the metals serve as donors to one or more ligands. The first examples of metal basicity date to the 1930's when Hieber and his coworkers prepared transition metal carbonyl hydrides and demonstrated their acidity. During this time Hieber and his school found that metal carbonyl anions may bring about nucleophilic displacements on inorganic and organic halides. About 20 years later, Wilkinson and his students initiated studies on the protonation of π-cyclopentadienyl complexes. This work, in which extensive use was made of proton nmr, stimulated much of the current interest in the protonation of transition metals. The scope of metal basicity has been significantly extended by the recent discovery of compounds in which the metal serves as a donor toward molecular Lewis acids such as BF_3, BH_3, O_2, SO_2, or tetracyanoethylene.

Nmr and infrared spectroscopy are important tools in the study of metal basicity. In particular a large high-field nmr shift is characteristic of hydrogen attached to a transition metal.[1] This technique is sensitive and in many instances is the only easy method to demonstrate the protonation of a metal. Diagnostic vibrational frequencies are provided by carbon monoxide and metal–halogen moieties, which are common in metal bases and Lewis acids, respectively. The CO stretching frequency, $\nu(CO)$, increases when the electron density on the central metal atom decreases.[2] Thus, when a carbonyl-containing complex serves as a base, an increase in $\nu(CO)$ is expected. Metal–halogen stretching frequencies are found to decrease when electron density on the metal atom increases. Therefore, when a metal (or metalloid) halide serves as acceptor, $\nu(MX)$ should decrease.[3]

It can be anticipated that metal basicity will become an increasingly important concept because current vigorous activity in the synthesis of new low oxidation-state complexes will lead to new metal bases and because available spectroscopic tools allow convenient recognition of metal base interaction with Lewis acids. Already the concept has proved useful for systematization of the chemistry and properties of many complexes. This Account will outline these systematics with special emphasis on the interaction of metal complexes with molecular Lewis acids such as BF_3, O_2, and tetracyanoethylene.

Metal–Proton Interaction[4]

Although carbonyl hydrides have been known for nearly 40 years, the thermodynamics of their proton dissociation has not been studied in detail because of the instability of these compounds. However, enough dissociation constant data are available to demonstrate some general trends. From Table I it is clear that basicity of the mononegative metal carbonyl anion decreases on going from Mn through Co, across the first transition metal period. Descending group VII from $HMn(CO)_5$ to $HRe(CO)_5$ leads to a large increase in basicity for the metal. Both of these trends are common in the basicity of transition metals toward a variety of reference acids but are the opposite of those found for main group bases.

Substitution of other ligands for CO has a significant influence on the basicity of metal carbonyl anions. Ligands like phosphines, which are better σ donors and poorer π back-bonders than CO, increase the basicity of the metal. For example, it may be seen in Table I that $HCo(CO)_3P(C_6H_5)_3$ has an acid dissociation constant about seven orders of magnitude lower than its parent, $HCo(CO)_4$. Similarly, $Fe(CO)_4(P(C_6H_5)_3)$ and $Fe(CO)_3(P(C_6H_5)_3)_2$ appear to be more strongly protonated than $Fe(CO)_5$ in acid media.[5]

Protonation of a metal carbonylate leads to a large structural reorganization of the complex. For example, the vibrational data for $Fe(CO)_4^{2-}$ and HFe-

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[1] G. Wilkinson, "Advances in The Chemistry of The Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 50.

[2] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 731.

[3] R. H. J. Clark, *Spectrochim. Acta*, **21**, 955 (1965); D. F. Shriver and M. P. Johnson, *Inorg. Chem.*, **6**, 1265 (1967); I. Wharf and D. F. Shriver, *ibid.*, **8**, 914 (1969).

[4] A detailed discussion of transition metal hydrides is given by A. P. Ginsberg in "Transition Metal Chemistry," Vol. 1, R. L. Carlin, Ed., Marcel Dekker, New York, N. Y., 1965, p 111.

[5] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

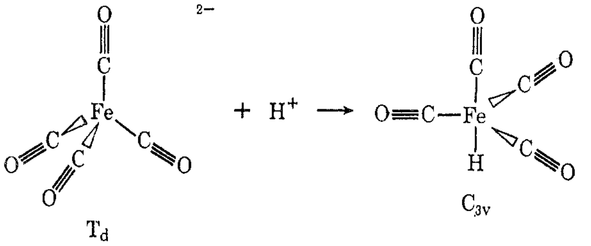
Table I

Acid Dissociation Constants and Shifts in ν(CO) for Some Metal Carbonyl Hydrides

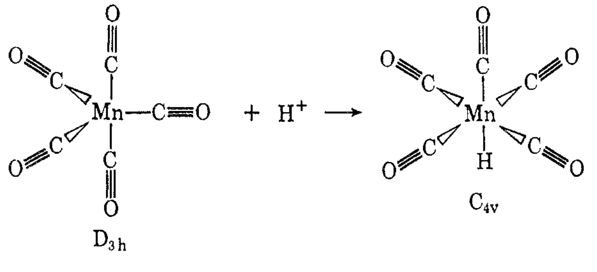
Compd	Acid dissn constant	$\Delta\nu$, cm^{-1} [a]
$HMn(CO)_5$	0.8×10^{-7} [b]	*Ca.* 159[c]
$H_2Fe(CO)_4$	4×10^{-5} (K_1)[d]	122[e]
	4×10^{-14} (K_2)	
$HCo(CO)_4$	*Ca.* 1[d]	175[e]
$HRe(CO)_5$	Very low[f]	*Ca.* 95[g]
$HCo(CO)_3P(C_6H_5)_3$	1.1×10^{-7} [d]	

[a] $\nu(CO)_{av}$ for protonated form minus $\nu(CO)_{av}$ for the metal base. Where complete assignments are available the average is based on frequencies weighted according to their degeneracy. Approximate $\Delta\nu$ values may be in significant error because of incomplete data. [b] Determined at 20°: W. Hieber and G. Wagner, *Z. Naturforsch. B*, **13,** 339 (1958). [c] Data from ref 6 and P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **89,** 2851 (1967). [d] Determined at 17.5°: W. Hieber and W. Hübel, *Z. Elektrochem.*, **57,** 235 (1953). [e] Data from ref 6. [f] W. Beck, W. Hieber, and G. Braun, *Z. Anorg. Allg. Chem.*, **308,** 23 (1961). [g] Data from D. M. Adams, D. J. Cook, and R. D. W. Kemmitt, *J. Chem. Soc. A*, 1067 (1968), and Braterman, *et al.*[c]

$(CO)_4^-$ suggest a rearrangement from tetrahedral to trigonal-bipyramidal symmetry (eq 1).[6] Similarly, vibrational data for $Mn(CO)_5^-$ and diffraction data for the corresponding hydride suggest a transformation from a trigonal-bipyramidal to an octahedral complex (eq 2).[6,7] By contrast, main group bases generally undergo relatively little change in geometry upon protonation (eq 3). This difference may be attributed to the low stereochemical activity of lone electron pairs in transition metal complexes, presumably because the multilobed d orbitals are adaptable to a variety of geometries.



(1)



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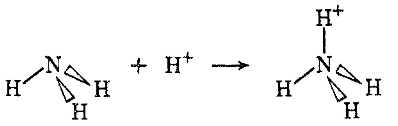

(3)

As expected from the discussion given in the introduction, vibrational data consistently show a large increase in average CO stretching frequency upon protonation of metal carbonyl anions (Table I) (eq 4, for example).

$$Co(CO)_4^- + H^+ = HCo(CO)_4 \qquad (4)$$
$$\nu(CO)_{av} = 1892\ cm^{-1} \qquad \nu(CO)_{av} = 2067\ cm^{-1}$$

Aside from the phosphine-substituted metal carbonyls, which have already been mentioned, metal basicity is displayed by other substituted carbonyls and carbonylates. A cross section of these bases is presented in Table II.

Table II

Some Substituted Metal Carbonyl Bases

Metal base	τ_{M-H}[a]	$\Delta\nu$(CO),[b] cm^{-1}	Basicity[c]
$(\pi\text{-}C_5H_5)Cr(CO)_3^-$ [d]	15.46		Medium
$(\pi\text{-}C_5H_5)Mo(CO)_3^-$ [d]	15.52	160	Medium
$(\pi\text{-}C_5H_5)W(CO)_3^-$ [d]	17.33	158	Medium
	11.93[e,f]		Weak
(cpylid)$Cr(CO)_3$[g]	15.09	142	Weak
(cpylid)$Mo(CO)_3$[g]	15.34	143	Weak
(cpylid)$W(CO)_3$[g]	17.15	143	Weak
$(\pi\text{-}C_6H_6)Cr(CO)_3$[f]	13.55		Weak
$(\pi\text{-}C_5H_5)Fe(CO)_2^-$ [d]	21.91[d]		Strong
$(\pi\text{-}C_5H_5)Ru(CO)_2^-$ [d]	20.92[d]		Strong

[a] Proton nmr for protonated form of metal base. [b] $\nu(CO)_{av}$ for protonated form minus $\nu(CO)_{av}$ for metal base. In these averages, frequencies are weighted according to their degeneracy. [c] Strong ≈ protonated by water; medium ≈ protonated by aqueous acetic acid; weak ≈ protonated by $BF_3 \cdot H_2O$ or similar acid medium. [d] A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963). [e] Diprotonated species. [f] Reference 5. [g] Reference 41; cpylid = $(C_6H_5)_3PC_5H_4$.

It was first shown by the protonation of biscyclopentadienyl complexes that carbon monoxide is not an essential ligand in basic metal complexes. For example, $(\pi\text{-}C_5H_5)_2MoH_2$, $(\pi\text{-}C_5H_5)_2WH_2$, and $(\pi\text{-}C_5H_5)_2ReH$ are easily protonated, and the iron group metallocenes are protonated in strong acids, such as $BF_3 \cdot H_2O$.[8,9] The difference in basicity is attributed to the greater interaction of metal electrons with the cyclopentadienyl rings in ferrocene-like systems than in the hydrides where the hydrogen ligands force the rings into a canted array.[10,11]

A number of metal–metal-bonded carbonyl derivatives are known to protonate.[5] In one of these systems, $(CO)_5Cr\text{–}H\text{–}Cr(CO)_5^-$, there is an indication from the symmetry, as determined by X-ray diffraction, that a linear Cr–H–Cr bridge is involved.[12] This may be regarded as a linear version of the three-center

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(6) The vibrational data of Edgell, *et al.*, and Stammerich, *et al.*, have been discussed by D. M. Adams, "Metal-Ligand and Related Vibrations," Edward Arnold, London, 1967, p 85 ff.

(7) S. J. LaPlaca, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8,** 1928 (1969). However, in contrast to the usual observation of hydrogen occupying a coordination site, R. W. Baker and P. Pauling, *Chem. Commun.*, 1495 (1969), find no obvious coordination site for H in $RhH(P(C_6H_5)_3)_4$.

(8) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

(9) T. J. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, *J. Amer. Chem. Soc.*, **82,** 5249 (1960).

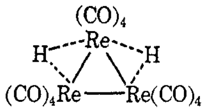
(10) C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, **15,** 1333 (1961); H. L. Lentzner and W. E. Watts, *Chem. Commun.*, 26 (1970).

(11) M. Gerloch and R. Mason, *J. Chem. Soc.*, 296 (1965).

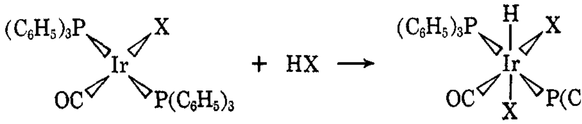
(12) L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *J. Amer. Chem. Soc.*, **88,** 366 (1966).

two-electron bond common in boron hydride chemistry. Consideration of tungsten hydrogen coupling in the nmr of $(\pi\text{-}C_5H_5)_2W_2(CO)_6H^+$, $(\pi\text{-}C_5H_5)_2MoW(CO)_6H^+$, $W_2(CO)_{10}H^-$, and $MoW(CO)_{10}H^-$ led to the conclusion that the proton in these systems may reside in either a bent or linear M–H–M arrangement,[13a] and some preference may be given to the linear configuration in view of the linear Cr–H–Cr bond mentioned above. However, a recent nmr study shows that the nmr results alone do not exclude structures involving a terminal hydrogen bonded to one of the metals.[13b]

The trinuclear rhenium hydride, $H_3Re_3(CO)_{12}$, and its partially deprotonated forms, $H_2Re_3(CO)_{12}^-$ and $HRe_3(CO)_{12}^{2-}$, provide further examples of M–H–M bonding which are substantiated by good physical evidence. For the mononegative anion X-ray diffraction and vibrational data indicate the structure[14]



From the standpoint of an acid–base interpretation, a more complicated example than those considered above is afforded by "oxidative addition" of an acid to a coordinatively unsaturated complex (eq 5, for example).

 (5)

This reaction may be viewed as the interaction of a metal with both an acid, H^+, and a base, X^-. However, Vaska discussed the reactions in terms of metal basicity,[15] which implies that the metal–proton interaction is dominant. A good illustration of the correctness of this view is afforded by a recent study in which it was shown that the extent of the reaction $HOOCR + IrCl(CO)(P(CH_3)_2C_6H_5)_2 \rightleftharpoons HIrCl(CO)(P(CH_3)_2C_6H_5)_2OOCR$ increases as the acidity of the carboxylic acid increases.[16] If the dominant mode of interaction were between carboxylate and Ir, one might expect the weakest acid to coordinate the most strongly. The utility of the metal base concept in systematizing many other oxidative addition reactions is extensively reviewed elsewhere.[17,18]

Metal–Lewis Acid Interaction[13a]

Heavy metal salts of metal carbonyl anions have been known for over 40 years. These may be regarded as metal base–metal acceptor complexes, an interpretation which is substantiated by the increase in $\nu(CO)$ from the carbonyl anion to the salt. Furthermore, these compounds undergo many acid displacement reactions (eq 6, for example).

$$H_2Fe(CO)_4 + HgCl_2 \longrightarrow Hg(Fe(CO)_4) + 2HCl \qquad (6)$$

Another illustration of simple base displacement is afforded by the partial dissociation of $Zn(Co(CO)_4)_2$, $Cd(Co(CO)_4)_2$, and $Hg(Co(CO)_4)_2$ in dimethylformamide solution.[19] This dissociation arises in part from competition between the basic solvent and $Co(CO)_4^-$ for coordination sites on the group II metal. As expected, the least dissociation takes place for the strongest acid–base combination, *viz.* $Hg(Co(CO)_4)_2$. Similarly, the transition metal base $Co(CO)_4^{2-}$ may be displaced from $Hg(Co(CO)_4)_2$ by the main group base Br^- (eq 7).[19]

$$Hg(Co(CO)_4)_2 + nBr^- \overset{DMF}{\rightleftharpoons} HgBr_n^{2-n} + 2Co(CO)_4^- \qquad (7)$$

The reverse of this, nucelophilic displacement of a ligand by a metal complex, is a reaction of considerable utility, which may be applied to the synthesis of many metal–metal-, metal–metalloid-, and metal–carbon-bonded compounds.[20-22] A few examples serve to illustrate the scope of this reaction

Halide displacement from a metalloid[23]

$$(C_6H_5)_2BCl + Mn(CO)_4P(C_6H_5)_3^- \rightleftharpoons (C_6H_5)_2B\text{–}Mn(CO)_4P(C_6H_5)_3 + Cl^-$$

Halide displacement from a boron hydride[24]

$$B_5H_8Br + Re(CO)_5^- \rightleftharpoons B_5H_8Re(CO)_5 + Br^-$$

Halide displacement from acetyl chloride[22]

$$CH_3COCl + Fe(CO)_2(\pi\text{-}C_5H_5)^- \rightleftharpoons CH_3COFe(CO)_2(\pi\text{-}C_5H_5) + Cl^-$$

Halide displacement from a metal[20]

$$(CH_3)_2SnCl_2 + 2Ir(CO)_3P(C_6H_5)_3^- \rightleftharpoons (CH_3)_2Sn(Ir(CO)_3P(C_6H_5)_3)_2 + 2Cl^-$$

Carbon monoxide displacement[25]

$$Cr(CO)_6 + Mn(CO)_5^- \rightleftharpoons (OC)_5Cr\text{–}Mn(CO)_5^- + CO$$

Tetrahydrofuran displacement[26]

$$Cr(CO)_5\cdot THF + (\pi\text{-}C_5H_5)_2WH_2 \rightleftharpoons (CO)_5CrW(\pi\text{-}C_5H_5)_2H_2 + THF$$

Halide displacement, which is illustrated in the first four reactions, accounts for the bulk of the literature reports of nucleophilic displacement by metal bases. While reactions of this type are generally discussed in terms of simple one-step nucleophilic displacement, more complex mechanisms may be involved in some cases. For example, the reaction of $Co(CN)_5^{3-}$

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(13) (a) J. C. Kotz, and D. G. Pedrotty, *Organometal. Chem. Rev., Sect. A*, **4**, 479 (1969); (b) G. M. Whitsides and G. Maglio, *J. Amer. Chem. Soc.*, **91**, 4980 (1969).

(14) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *ibid.*, **90**, 7135 (1968).

(15) L. Vaska and J. W. DiLuzio, *ibid.*, **84**, 679 (1962).

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

(17) L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).

(18) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 53 (1968).

(19) J. M. Burlitch, *J. Amer. Chem. Soc.*, **91**, 4562, 4563 (1969).

(20) M. C. Baird, *Progr. Inorg. Chem.*, **9**, 1 (1968); J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Amer. Chem. Soc.*, **88**, 5035 (1966).

(21) N. S. Vyazankin, G. A. Razuvaev, and O. A. Kruglaya, *Organometal. Chem. Rev., Sect. A*, **3**, 323 (1968).

(22) R. B. King, *Advan. Organometal. Chem.*, **2**, 157 (1964).

(23) H. Nöth and G. Schmid, *Z. Anorg. Allg. Chem.*, **345**, 69 (1966).

(24) D. F. Gaines and T. V. Irons, *Inorg. Chem.*, **7**, 1041 (1968).

(25) U. Anders and W. A. G. Graham, *J. Amer. Chem. Soc.*, **89**, 539 (1967).

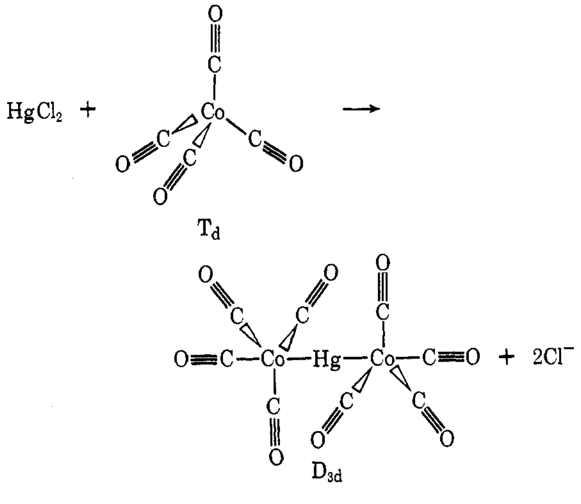
(26) B. Deubzer and H. D. Kaesz, *ibid.*, **90**, 3276 (1968).

with alkyl halides proceeds by a stepwise radical mechanism.[27]

$$Co(CN)_5^{3-} + RX \longrightarrow Co(CN)_5X^{3-} + R\cdot$$

$$Co(CN)_5^{3-} + R\cdot \longrightarrow Co(CN)_5R^{3-}$$

As with the protonation of carbonylate ions, most of these reactions involve a large rearrangement of the ligands attached to the metal base (eq 8, for example).[6] In a kinetic study, it was found that Co(I) in vitamin B_{12s} or cobaloximes is the strongest known nucleophile.[28] Another quantitative study shows that nucleophilicity increases as one descends groups VI and VII. Thus the second-order rate constant for reaction with methyl iodide follows the order: $(\pi\text{-}C_5H_5)Cr(CO)_3^- < (\pi\text{-}C_5H_5)Mo(CO)_3^- < (\pi\text{-}C_5H_5)W(CO)_3^-$, and $Mn(CO)_5^- < Re(CO)_5^-$.[29] However, for the iron–ruthenium pair in group VIII the opposite trend is observed, since the second-order rate constant is nearly an order of magnitude larger for the reaction for $(\pi\text{-}C_5H_5)Fe(CO)_2^-$ with C_2H_5Br than for the analogous reaction of $(\pi\text{-}C_5H_5)Ru(CO)_2^-$. This decrease in basicity upon going down the iron group has a parallel in the apparently greater basicity of $(\pi\text{-}C_5H_5)_2Fe$ than $(\pi\text{-}C_5H_5)_2Ru$ toward H^+ as a reference acid. The log k_2 values for the above-mentioned displacement reactions give a good linear correlation with oxidation potentials of the transition metal nucleophiles. A correlation of this type is typical in main group chemistry.[30]



(8)

As already mentioned, many nucleophilic displacements may proceed *via* simple adduct intermediates or transition states, analogous to those written for SN2 substitution on carbon. Therefore, the formation of simple adducts between metal bases and coordinatively unsaturated Lewis acids such as mercuric halides or boron halides is closely related to the foregoing nucleophilic displacement reactions. The most thoroughly characterized example is provided by the complex between $(\pi\text{-}C_5H_5)Co(CO)_2$ and $HgCl_2$ which is known from an X-ray diffraction study to contain a Co–Hg bond and to have both chlorides associated with the mercury (Figure 1).[31,32] In keeping with the frequency shifts expected for donation of electron density from Co to Hg, the formation of this complex is accompanied by an increase of *ca.* 50 cm^{-1} in ν(CO) and a decrease of *ca.* 100 cm^{-1} for the average ν(HgCl). In *o*-chloroaniline the affinity for $(\pi\text{-}C_5H_5)Co(CO)_2$ falls in the order $HgCl_2 > HgBr_2 > HgI_2$. Another series of adducts may be formed each of which contains 2 mol of mercuric halide/mol of the cobalt complex. On the basis of far-infrared spectra it is thought that the second mole of mercuric halide is uncoordinated.

Similarly, the reaction of mercuric chloride or bromide with $(\pi\text{-}C_5H_5)M$(diolefin) (M = Co or Rh and diolefin = 1,5-cyclooctadiene or norbornadiene) yields 1:1 complexes.[31] The Hg–Cl stretching frequencies of these are similar to those found for the cobalt carbonyl derivative mentioned above, and thus it is likely that the adducts involve electron pair donation to mercury dihalide.

The major problem in formulating structures for many of the mercuric halide complexes is whether or not the halide ion has been displaced. Classical approaches, such as conductance, are of limited utility because of the lability and/or low solubility of the adducts in suitable solvents. Another complication is the frequenct occurrence of adducts containing 2 mol of mercuric halide/mol of transition metal base. For example, $(\pi\text{-}C_5H_5)Co(CO)_2\cdot 2HgX_2$, which has already been mentioned, is thought to contain one uncoordinated HgX_2, while $(diphos)_2Mo(CO)_2\cdot 2HgCl_2$ has been formulated as $[(diphos)_2Mo(CO)_2HgCl^+][HgCl_3^-]$.[33] Despite these complications, there are several mercuric halide complexes in addition to $(\pi\text{-}C_5H_5)Co(CO)_2\cdot HgCl_2$ which are reasonably described as simple adducts: $(\pi\text{-}C_5H_5)Rh(CO)_2\cdot HgCl_2$,[34] $(\pi\text{-}C_6H_3(CH_3)_3)Mo(CO)_3\cdot HgCl_2$,[33] $RhCl(1,5\text{-}C_8H_{12})_2\cdot 2HgCl_2$,[35] and $Fe(CO)_3(P(C_6H_5)_3)_2\cdot HgCl_2$.[36] The last of these is formulated as a simple adduct while the ruthenium and osmium analogs are 1:2 complexes for which the ionic structure $[M(CO)_3L_2HgX^+][HgX_3^-]$ has been assigned. In summary the mercury halide complexes may involve (1) complete displacement of halide to produce metal–mercury–metal bonds, (2) partial halide displacement to yield complexes of HgX^+, or (3) retention of both halides to produce simple adducts of HgX_2. While the data are still fragmentary, the strongest metal bases appear to promote the first type of reaction and the weakest tend to favor the last.

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[27] J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, **87**, 5361 (1965).

[28] G. N. Schrauzer, E. Deutsch, and R. J. Windgassen, *ibid.*, **90**, 2441 (1968).

[29] R. E. Dessey, R. L. Pohl, and R. B. King, *ibid.*, **88**, 5121 (1966).

[30] J. O. Edwards, *ibid.*, **76**, 1540 (1954); **78**, 1819 (1956).

[31] D. J. Cook, J. L. Daws, and R. D. W. Kemmitt, *J. Chem. Soc. A*, 1547 (1967).

[32] I. M. Nowell and D. R. Russell, *Chem. Commun.*, 817 (1967).

[33] diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$: K. Edgar, B. F. G. Johnson, J. Lewis, and S. B. Wild, *J. Chem. Soc. A*, 2851 (1968).

[34] J. L. Daws and R. D. W. Kemmitt, *ibid.*, *A*, 1073 (1968).

[35] J. L. Daws and R. D. W. Kemmitt, *ibid.*, *A*, 2093 (1968).

[36] See Adams, *et al.*, Table I, footnote *g*.

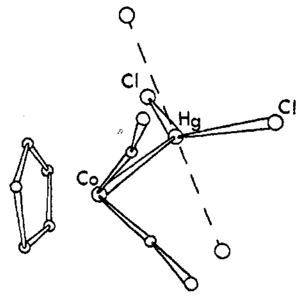


Figure 1. The structure of $(C_5H_5)Co(CO)_2 \cdot HgCl_2$.[32] Weak coordination to the chlorides of adjacent molecules is indicated by dashed lines.

Group III Lewis acids such as BF_3 display relatively simple chemistry and therefore are excellent prototypes for Lewis acid–base interaction. For example, halide displacement is less common with BF_3 than with mercury dihalides. The first reports of boron–metal adducts involve the formation of $(\pi\text{-}C_5H_5)_2WH_2 \cdot BF_3$ in our laboratory[37] and the formation of $Re(CO)_5 \cdot BH_3^-$ and similar species by Parshall.[38] In both cases the parent metal bases are known to protonate. The analogous $(\pi\text{-}C_5H_5)_2MoH_2$ and $(\pi\text{-}C_5H_5)_2ReH$ also display Lewis basicity toward boron halides, and in each case the characteristic decrease in B–X stretching frequency is observed upon adduct formation.[39] While these boron halide adducts are insoluble in nondestructive solvents, Brunner, Wailes, and Kaesz were able to study the more soluble aluminum trimethyl adducts, $(\pi\text{-}C_5H_5)_2WH_2 \cdot Al(CH_3)_3$ and $(\pi\text{-}C_5H_5)_2ReH \cdot Al(CH_3)_3$, in solution,[40] where the nmr results are most easily interpreted in terms of metal–metal adduct formation.

Metal basicity was not observed for $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ or $(\pi\text{-}C_5H_5)W(CO)_3^-$ because of complicating side reactions.[39] However, a related series of metal bases have been successfully investigated by Kotz and Pedrotty who found that basicity toward BF_3 increases in the order: (cpylid)$Cr(CO)_3$ < (cpylid)$Mo(CO)_3$ < (cpylid)$W(CO)_3$.[41] As expected, ν(CO) is greatly increased on adduct formation and ν(B–F) is decreased. These metal bases form stronger adducts with BCl_3 than BF_3, which parallels the order of affinity found with main group bases. However, in contrast to main group bases biscyclopentadienyl metal hydrides and cpylid metal tricarbonyls fail to add BH_3. The greater stability of BF_3–metal bonds than BH_3–metal bonds has its parallel in the generally increased stability of CF_3–transition metal compounds over their CH_3 analogs.

The only report of metal–BH_3 adducts is that of Parshall, who found that basicity toward BH_3 like that toward the proton increases from manganese to rhenium, $Mn(CO)_5^- < Re(CO)_5^-$,[38] and decreases from group VII to group VIII, $Mn(CO)_5^- > Co(CO)_4^-$. Another similarity is the increase in basicity toward BH_3 upon substitution of triphenylphosphine for carbon monoxide, *viz.*, $Mn(CO)_5^- < Mn(CO)_4P(C_6H_5)_3^-$. Coordination of the metal carbonyl anions to BH_3 has relatively little influence on the average ν(CO). Apparently, electron density on the metal is not substantially changed by adduct formation with BH_3.

The halides of aluminum, gallium, and indium are stronger Lewis acids than BH_3 and therefore they might be expected to form complexes with metal bases. However, as with mercury halides the displacement of halide ion occurs readily. For example, the reactions of $Fe(CO)_4^{2-}$ or $Co(CO)_4^-$ with $GaBr_3$ or $InBr_3$ reveal a delicate balance between simple adduct formation and nucleophilic displacement of halide.[42] Ruff observed the formation of a simple adduct in reaction 9, whereas Patmore and Graham

$$[((C_6H_5)_3P)_2N][Co(CO)_4] + InBr_3 \xrightarrow{CH_2Cl_2} [((C_6H_5)_3P)_2N][Co(CO)_4 \cdot InBr_3] \quad (9)$$

had previously observed halide displacement when a different cation and solvent were employed (eq 10).[43]

$$2Na[Co(CO)_4] + InBr_3 \xrightarrow{THF} InBr(Co(CO)_4)_2 \cdot THF + 2NaBr\downarrow \quad (10)$$

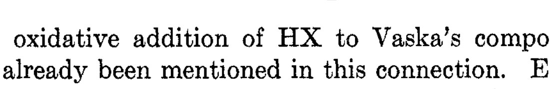
Apparently the insolubility of NaBr in the latter reaction serves as a driving force for halide displacement. Interestingly, $Fe(CO)_4^{2-}$, which is more basic than $Co(CO)_4^-$, promotes halide displacement in a homogeneous system (eq 11).[42] A combination of

$$Fe(CO)_4InBr_3^{2-} \rightleftharpoons Fe(CO)_4InBr_2^- + Br^- \quad (11)$$

even greater metal basicity and insolubility of NaCl may account for the displacement of Cl^- from $GaCl_3$ by $NaMn(CO)_5$ (eq 12).[44] In keeping with the interpretation of these reactions in terms of transition metal basicity, complex formation with the group III halide is accompanied in all cases by a significant increase in ν(CO).

$$GaCl_3 + NaMn(CO)_5 \xrightarrow{THF} Mn(CO)_5GaCl_2 \cdot THF + NaCl\downarrow \quad (12)$$

Square-planar d^8 complexes are attractive for metal basicity studies because of the open coordination sites and available electron density in the d_{z^2}, d_{xz}, and d_{yz} orbitals



The oxidative addition of HX to Vaska's compound has already been mentioned in this connection. Early studies on the interaction of square-planar Ni(II) com-

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[37] D. F. Shriver, *J. Amer. Chem. Soc.*, **85**, 3509 (1963).
[38] G. W. Parshall, *ibid.*, **86**, 361 (1964).
[39] M. P. Johnson and D. F. Shriver, *ibid.*, **88**, 301 (1966).
[40] H. Brunner, P. C. Wailes, and H. D. Kaesz, *Inorg. Nucl. Chem. Lett.*, **1**, 125 (1965).
[41] cpylid = $(C_6H_5)_3PC_5H_4$: J. C. Kotz and D. G. Pedrotty, *J. Organometal. Chem.*, in press.
[42] J. K. Ruff, *Inorg. Chem.*, **7**, 1499 (1968).
[43] D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 1586 (1966).
[44] S. Onaka, T. Iwamoto, and Y. Sasaki, *Bull. Chem. Soc. Jap.*, **41**, 1033 (1968).

plexes with Lewis acids led to reactions with the ligands but not the metal.[45,46] However, more recent studies on Rh(I) and Ir(I) square-planar complexes demonstrate the formation of metal–boron adducts.[47–49] One of these complexes, Vaska's compound $IrCl(CO)(P(C_6H_5)_3)_2$, has been studied in some detail.

Vaska's compound forms both 1:1 and 1:2 adducts with BF_3. The former appears to be a simple $Ir-BF_3$ adduct since its formation results in a 100-cm^{-1} increase for $\nu(CO)$ and a decrease in $\nu(BF_3)$. At room temperature the dissociation pressure of BF_3 above the adduct is quite low, but main group bases such as triethylamine will displace BF_3 from the metal. In a study of homogeneous equilibria between various phosphine-substituted analogs of Vaska's compound and $B(C_6F_5)_3$, it was found that the most basic phosphine ligands produce a larger formation constant. It is likely that inductive effects are responsible for this increase in basicity; however, steric factors may also play a role since the most basic phosphines were also the least bulky.[49]

Of particular interest are parallels which may be drawn between the 1:1 BF_3 adducts of Vaska's compound and a variety of other molecular adducts. When $\nu(CO)$ is plotted against electron affinity, EA, for the added molecules, O_2, SO_2, tetracyanoethylene, and BF_3, a monotonic and nearly linear increase of $\nu(CO)$ with increasing EA is observed.[48] This correlation, which encompasses both the free parent $IrCl(CO)(P(C_6H_5)_3)_2$ and its BF_3 adduct, indicates that the predominant mode of interaction is metal-to-ligand donor–acceptor interaction for all of the molecules.

Similarly, much of the chemistry for simple adducts of Vaska's compound may be understood in terms of the strongest acceptors forming the most stable adducts.[17,48,49] For example, O_2 and SO_2, which have low electron affinities and are poor acceptors toward main group bases, form adducts with relatively high dissociation pressures, while the stronger Lewis acid BF_3 does not display a noticeable dissociation pressure. Another example is afforded by the greater affinity of Vaska's compound for C_2F_4 than C_2H_4.

Structural data also agree with the metal–base model for these compounds. For example, SO_2 is attached so that the normal to the plane of the SO_2 makes a 32° angle with the S–Ir bond.[50] This geometry may be rationalized by invoking an approximately sp^3-hybridized vacant acceptor orbital on sulfur.[51,52] In agreement with this explanation, the trimethylamine–SO_2 adduct, which must involve nitrogen-to-sulfur electron donation, is found to have a 22° angle between the normal to the SO_2 plane and the N–S bond.[53] Similarly a bent Ir–NO bond was found in $IrCl(CO)(P(C_6H_5)_3)_2 \cdot NO^+$ and was explained in terms of $Ir \rightarrow NO^+$ bonding.[51] In both SO_2 and NO^+ adducts a slight reorganization of the metal base system is observed upon adduct formation. For example, in the NO^+ adduct the N–Ir–Cl and N–Ir–C bond angles are distinctly greater than 90° (101 and 97°, respectively).[51]

The multicenter Lewis acids, O_2 and tetracyanoethylene, exhibit significant increases in O–O and central C–C bond lengths upon coordination to Ir(I).[54–56] This bond lengthening is expected for the donation of electron density into π^* orbitals of these π acids. However, an increase in bond length does not prove the metal base model since ligand-to-metal donation would give a similar results. As may be seen in Figures 2 and 3, these multicenter Lewis acids cause significant reorganization of the square-planar $IrX(CO)L_2$ moiety.

Early discussions of the bonding in substituted ethylene, O_2, and SO_2 adducts have stressed dualistic bonding models in which electron donation from the ligand and back π bonding to the ligand are both important. The prototypes of such bonding descriptions are those applied to CO,[57] ethylene,[58,59] and O_2[60] complexes. However, as outlined above, the Ir(I) and Rh(I) complexes appear to bond primarily as donors to $C_2(CN)_4$, O_2, and SO_2 molecules, and it is probable that this is the best first approximation to the bonding of these molecules with other low-oxidation-state metals.

In a broader sense, ligands such as H_2O and NH_3 are donors, PF_3, CO, and C_2H_4 simultaneously exhibit both donor and acceptor interaction, and H^+ and BF_3 are pure acceptors. There are no sharp distinctions between these classes, and the best category for a ligand may vary with the electronic structure of the central metal atom. It is to be expected that metals in low oxidation states will be the most basic while those in higher oxidation states will have increased acid character. In keeping with this idea, the $Ru(II)-SO_2$ skeleton has been found to be planar, presumably owing to the favorable situation this creates for both σ donation and back π bonding.[61]

In contrast to the formation of a stable BF_3 adduct, Vaska's compound does not have an appreciable affinity for BH_3. Since a similar preference of other

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(45) G. N. Schrauzer, *Ber.*, **95**, 1438 (1962).

(46) D. F. Shriver, *J. Amer. Chem. Soc.*, **84**, 4610 (1962); **85**, 1405 (1963).

(47) P. Powell and H. Nöth, *Chem. Commun.*, 637 (1966).

(48) R. N. Scott, D. F. Shriver, and L. Vaska, *J. Amer. Chem. Soc.*, **90**, 1079 (1968); D. F. Shriver, M. P. Johnson, R. N. Scott, and J. F. Jackovitz, *Proc. Int. Conf. Coord. Chem., 9th*, 248 (1966).

(49) R. N. Scott, D. F. Shriver, and D. Lehman, *Inorg. Chim. Acta*, in press.

(50) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **5**, 405 (1966).

(51) D. J. Hodgson and J. A. Ibers, *ibid.*, **7**, 2345 (1968).

(52) K. W. Muir and J. A. Ibers, *ibid.*, **8**, 1921 (1969), find a similar geometry for the rhodium analog.

(53) D. Vander Helm, J. D. Childs, and S. D. Christian, *Chem. Commun.*, 887 (1969).

(54) S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 2581 (1965).

(55) J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968).

(56) L. Manojlović-Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, **47**, 84 (1969).

(57) L. Pauling, "Nature of The Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1948, p 251.

(58) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951).

(59) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(60) J. S. Griffith, *Proc. Roy. Soc., Ser. A*, **235**, 23 (1956).

(61) L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).

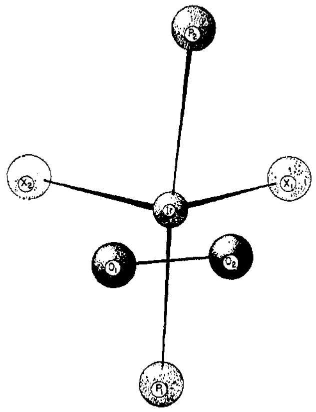
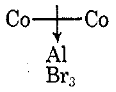


Figure 2. The structure of $IrClCO(P(C_6H_5)_3)_2 \cdot O_2$.[54] For clarity only the first coordination sphere is shown. X_1 and X_2 represent CO and Cl which could not be distinguished because of disorder.

metal bases for the hard Lewis acid, BF_3, has been noted previously in this Account, it might be inferred that these metals are hard bases.[62] However, this interpretation is confused by the high affinity of Ir(I) and Rh(I) for tetracyanoethylene and similar soft acids. Apparently the hard–soft classification is less useful with this transition metal base than with main group bases.

The rhodium analog of Vaska's compound, $RhClCO(P(C_6H_5)_3)_2$, has a low affinity for BF_3 but forms a stable BCl_3 adduct.[47,48] This order of stability is well established with main group bases, toward which BCl_3 is the stronger acid. In line with its low affinity for BF_3 the rhodium complex does not add O_2. The increase in basicity from Rh(I) to Ir(I) follows the usual trend going down a transition metal group.

Finally, multicenter metal bases deserve mention even though their chemistry is not well developed. In 1958 Chini and Ercoli observed the formation of $Co_2(CO)_8 \cdot AlBr_3$ and postulated a three-center interaction in which the aluminum accepts electrons from the metal–metal bond.[63] Detailed studies are hampered by the high reactivity of this compound; however, the infrared spectrum is reported[64] to be similar to that of the $Co_2(CO)_8$ parent.



$$\underset{\underset{Br_3}{Al}}{Co\overset{}{\underset{\downarrow}{—}}Co}$$

Recent work on $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ with boron halides has revealed several systems which may involve metal–metal bonds serving as donors. For example, the reversible formation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \cdot BF_3$ coupled with the increase in $\nu(CO)$ and decrease in $\nu(BF_3)$ indicate a metal base system.[65] Several more stable adducts have been isolated: $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \cdot BCl_3$, $[(\pi\text{-}C_5H_5)Fe(CO)]_4 \cdot 2BF_3$, and $[(\pi\text{-}C_5H_5)Fe(CO)]_4 \cdot 2BCl_3$.[66] In addition to the usual vibrational characterization, molecular weight data for the BCl_3 complexes agree with the simple metal base formulation; however, a definite statement concerning the bonding in these complexes must await the completion of current X-ray diffraction studies.

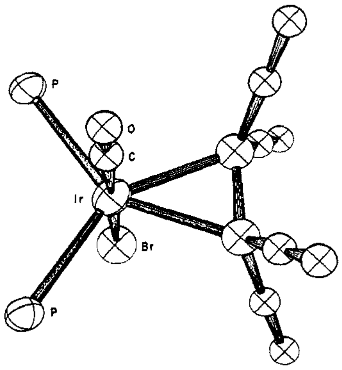


Figure 3. The structure of $IrClCO(P(C_6H_5)_3)_2 \cdot C_2(CN)_4$.[55] Phenyl groups are omitted for clarity.

Conclusions

Metal basicity is a useful concept for systematization of the chemistry and vibrational spectra of many low-oxidation-state metal complexes in combination with ligands such as H^+, BF_3, O_2, and tetracyanoethylene. Many similarities are observed with main group bases, and the following generalizations apply. (1) Low oxidation states promote metal basicity. Of the examples considered in this review the majority can be assigned 1+, 0, or negative oxidation state. (2) Electron-donating ligands increase metal basicity. The most frequently encountered examples involve replacement of CO by a phosphine, with a resulting increase in metal basicity. (3) Transition metal basicity generally increases going down a group. This trend is the opposite of that found for main group bases. Some iron group bases are exceptions to this rule, and other exceptions may be uncovered in more thorough research on metal basicity. (4) Significant structural changes frequently occur upon Lewis salt formation. Examples include the gross changes in geometry which occur upon protonation or heavy metal complexation of metal carbonyl anions and structural changes in Vaska's compound associated with the addition of O_2 or tetracyanoethylene.

Intensive study of low-oxidation-state transition metal complexes is very recent. Therefore it can be anticipated that the concept of metal basicity will continue to increase in importance as more of these potential metal base systems are discovered. The structural and (vibrational) spectroscopic implications of metal basicity are fairly well understood, but mechanistic implications have received little attention, and this area seems ripe for development. For example, the concept should prove useful in many oxidative and simple substitution reactions, similar to the known substitution of SO_2 for C_2H_4 in a Rh(I) complex.[67] Also,

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(62) R. G. Pearson, *Science*, **151**, 172 (1966).

(63) P. Chini and R. Ercoli, *Gazz. Chim. Ital.*, **88**, 1170 (1958).

(64) F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.*, 1882 (1960).

(65) K. Triplett, unpublished observations, Northwestern University.

(66) N. Nelson, unpublished observations, Northwestern University.

(67) R. Cramer, *J. Amer. Chem. Soc.*, **89**, 5377 (1967).

Lewis salts may be important as intermediates or transition states in catalytic reactions. An example in this category is the catalysis of CO exchange with $Fe(CO)_4P(C_6H_5)_3$ *via* an acidic medium.[68]

(68) F. Basolo, A. T. Brault, and A. J. Poë, *J. Chem. Soc.*, 676 (1964).

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The "Solid-State" Properties of Rigid Organic Solutions

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Long ago it was found that a variety of crystalline, inorganic solids were capable of slowly releasing stored energy in the form of visible light after irradiation in the visible or ultraviolet region or at the much higher energies of X-rays and γ-rays. These solids came to be known as crystal phosphors or simply "phosphors."[1] Not only do such sensitized solids exhibit afterglow, but they can also be photoconductive. Furthermore, the release of the stored energy can be variously hastened or retarded by the application of stimuli such as heat, infrared light, or electric fields. The modern theory of ordered solids, including impurity centers or defects, manages to embrace this class of crystalline materials quite successfully. What is quite remarkable is that over the past decade or so there has emerged a class of amorphous, organic solids having properties almost identical with those of the inorganic crystal phosphors.

These organic solids normally consist of simple dilute organic solutions which are converted to a rigid but noncrystalline state by cooling. Alternatively, polymerization into a rigid state is possible. Sensitization can be accomplished, as before, by high-energy irradiation or by photoexcitation. In the former case it is principally the solvent molecule which captures the energy, simply because it constitutes the bulk of the material. Photoexcitation is much more selective and occurs *via* the solute molecule whose spectrum normally appears at wavelengths to the red of the solvent absorption. In either case it seems that a large amount of the energy is stored through ionization or the separation of charges within the solids (an internal photoelectric effect).

The recombination of charges can lead to excited electronic states which may decay by radiative means giving rise to the "afterglow" of organic phosphors. Usually the afterglow is a luminescence characteristic of the solute molecule. Even in the case where the solvent is the primary absorber, solute emission can be seen because positive "holes" in the solvent are often mobile. When these are captured by the neutral solute molecule, the sensitized solid becomes similar to that in which the solute molecule is directly photoionized.

As we have indicated, these sensitized organic solids exhibit the full array of phosphor-like properties. These include photoconductivity, thermoluminescence (recombination luminescence seen upon heating), photostimulated emission (enhanced recombination luminescence through infrared or visible illumination), and electric stimulation (perturbation of the recombination luminescence by an externally applied electric field). The afterglow itself, seen at a given, fixed temperature, is conveniently called isothermoluminescence (ITL).

A nomenclature for these phosphor-like properties has developed which attempts to distinguish the two types of primary energy storage steps. Thus, when the activation step is by high-energy irradiation, the term "radio" appears somewhere in the name, whereas with visible or ultraviolet illumination, "photo" is used. Unfortunately, consistent rules have not been applied. Thus "radiophotoluminescence" is a luminescence released by photostimulation of a solid which has been previously sensitized by high-energy radiation. On the other hand electrophotoluminescence is the luminescence seen when an electric field is applied to a solid previously sensitized by ultraviolet illumination. Were the solid sensitized by high-energy irradiation one could use the term electroradioluminescence.

A number of laboratories have been active in studying the phosphor-like properties of irradiated organic solids (including polymers) during the past decade. In our own laboratory, we have been preoccupied with what we feel is a prototype rigid organic solution. The system consists of a solution of $\sim 10^{-3}$ *M* N,N,N',N',-tetramethyl-*p*-phenylenediamine (TMPD) in the solvent 3-methylpentane (3-MP) at 77°K. Our interest in this system arose from the early work on polarized photoionization (photodichroism) of rigid organic solutions carried out in the laboratories of Lewis at Berkeley in the 1940's.

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[1] For a survey of the field of inorganic, crystalline phosphors a useful reference is P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, New York, N. Y., 1949, Chapter VII.