Correspondence

Further Comments on the Loss of Hydrogen Molecules in the Mass Spectra of Transition Metal π Complexes

AIC407079

Sir:

In a recent publication, Innorta, Pignataro, and Natile[1] discussed the loss of small neutral molecules in the mass spectral fragmentation of transition metal compounds complexed to organic rings. In their study of the complex π-tetrahydronaphthalenenonacarbonyltetracobalt they suggested that only fragmentation processes of low activation energy are able to compete with metal decarbonylation and this accounts for the fragmentation of the organic ligand in ions of the type $[(C_{10}H_{12})Co_4(CO)_n]\cdot^+$ by loss of H_2 rather than H·, whereas the molecular ion of the free tetrahydronaphthalene exhibits extensive loss of the radical. Such an approach to the fragmentation of complexes of this type is extremely attractive and it seems to us that such arguments have a greater validity than ones that present a rationalization simply on the basis of the formation of extra π bonds between the metal atom and newly formed centers of unsaturation.[2]

Nevertheless, to our mind such an energetic explanation is only completely satisfactory in cases where the loss of some carbon monoxide molecules by the molecular ion precedes any fragmentation of the organic ligand. Such losses would undoubtedly reduce the internal energy of the daughter ions and under such circumstances it seems reasonable that the high-energy process of radical loss would be unable to compete with fragmentation by loss of H_2 or further molecules of CO. However, several examples are known[2b,3] in which loss of H_2 is observed from the molecular ions of complexes of the type $(\pi\text{-c-RC}_6H_7)Fe(CO)_3$ (R = 3'-acetylacetonyl, 2'-dimedonyl, 3'-indolyl, and 1'-*sym*-trimethoxybenzene) and this is the only process able to compete with decarbonylation. In the case of one of these (R = 2'-dimedonyl (dimedonyl = 5,5-dimethylcyclohexa-1,3-dione)), I, the mass spectrum of the free ligand II shows that the process $P\cdot^+ \rightarrow (P - 1)^+$ is the most favored mode of fragmentation of this molecular ion.[2b] Thus, this marked difference in behavior of the free ligand and complex cannot be adequately rationalized in terms of the parent ion of the latter only having sufficient internal energy to fragment by low-energy pathways.

It therefore appears that other factors may be important in this case and we suggest that the approach of McLafferty[4] provides a satisfactory rationale. McLafferty has adopted a different approach to the decomposition of molecular ions by competing reactions and suggested that the factors which play important roles in such considerations are (1) the relative stability of the various bonds in the decomposing ion, (2) the relative stabilities of the ionic and neutral products which could be formed by the competing degradation paths, and (3) the relative probability of a cyclic transition state being achieved for decomposition via concerted bond cleavage. It seems to us that one can rationalize the differences outlined for I and II above in terms of the second and third of these factors.

The results of ionization potential studies on organo-(transition metal) complexes indicate that the electron removed in the ionization process is of principally metal d character and thus the preferential site of charge location in the molecular ions of such complexes is the central metal atom.[5] This immediately suggests a difference in the nature of the free-ligand molecular ion and the complexed ligand in the molecular ion of the organometallic compound. The former is an odd-electron species, whereas the organic moiety of the latter may be classed as even electron, the radical site being located on the metal atom. McLafferty pointed out: "The most useful initial indication of fragment stability is classification as 'even-electron' or 'odd-electron'. The even-electron fragment, whether ion or neutral, usually has the much greater stability and therefore the greater influence on the course of the degradation reactions, with the odd-electron product showing only secondary influence. This does not mean, however, that odd-electron ions cannot be the most abundant in the spectrum, but in such cases other dominant factors are usually in effect." We have previously discussed the fragmentation of complexes of the type $(\pi\text{-c-}C_8H_7R)Fe(CO)_3$ in terms of such considerations[6] and believe that this approach has a wide, although not universal, application to the mass spectra of transition metal π complexes. [The fragmentation of complexes of the type $(C_6H_5COOR)Cr(CO)_3$ by loss of OR·[7] is an exception to this generalization. We believe this is most probably a consequence of the fact that the arene ring is well suited to stabilize the positive charge by resonance delocalization.[8]]

Thus the molecular ion of the free ligand (e.g., II) will undergo preferential radical loss producing an even-electron daughter ion, while the complexed ligand decomposes from an even-electron situation (with respect to the organic moiety) yielding an even-electron neutral species (H_2) and retaining the even-electron character of the organic moiety in the daughter ion. Alternatively, one could view this last fragmentation as $[(\pi\text{-}C_6H_7R)Fe(CO)_3]\cdot^+$ (odd-electron molecular ion) yielding $[(C_6H_5R)Fe(CO)_3]\cdot^+$ (odd-electron daughter ion) which in terms of McLafferty's approach is dominated by the factor that the metal atom is acting as a stabilizing feature for the radical site.

Furthermore, we believe that an important factor in the fragmentation of cyclohexadiene complexes is that not only is the daughter ion even-electron with respect to the organic moiety, but this organic moiety is a 6π system. The stability of formally aromatic ions in organic mass spectrometry is, of course, evidenced by the facility with which a wide range of aromatic compounds yield tropylium ions.[4]

Finally, it is worthy of reemphasis that Whitesides and Arhart[2a] have found that *endo,endo*-5,6-dideuterio-cyclohexa-1,3-dienetricarbonyliron exhibits a highly stereospecific loss of D_2 over H_2 and it may be that the metal atom plays a significant role in this aromatization process in accepting hydrogen atoms from the organic ligand prior to elimination of H_2.

To summarize, therefore, we are in no way casting doubt on the energetic approach employed by Innorta, Pignataro, and Natile and agree with these authors that activation energies must be of major importance in the fragmentation of metal π complexes. However, we do suggest that in certain cases, rationalization of the mass spectral behavior can only be achieved by also considering the stability of the products of possible decomposition paths and should also take account of the ability of the metal atom to participate in decompositions involving rearrangement. We are, of course, aware that the concept of charge localization at the metal atom is not without precedent in studies of the mass spectra of inorganic complexes[2b,9] but feel that its reemphasis is timely, and if this letter acts as a spur to other workers, if only to challenge its generality, it will have served its purpose.

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References and Notes

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Formation of Model Compounds of Biological Molybdenum(IV)

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Sir:

Because of a long-term interest in the chemistry of biological molybdenum,[1] the recent report of Selbin and coworkers[2] concerning the formation of a series of molybdenum(IV)–flavin compounds came to our attention. In their paper the Selbin group concluded that the isolated compounds are in the form of molybdenum(IV)–flavin complexes with the molybdenum in an anion group and the flavin as a protonated cation, $(HFl^+)(Mo^{IV}OCl_3^-)$. This conclusion is based on elemental analyses, differential thermal analyses, thermogravimetric analyses, infrared spectra, uv–visible spectra, NMR spectra, and ESR measurements.

The proposition that a complex is formed between $Mo^{IV}OCl_3^-$ and HFl^+ is in conflict with the results of Hemmerich and coworkers.[3] The latter group did not observe any interaction between flavin molecules and metal ions in acidic media. The Hemmerich group also observed that molybdenum(V) interacts with flavin molecules in acetonitrile to give a charge-transfer complex of a molybdenum(VI)–flavin anion radical with an absorption maximum at 406 nm. When zinc(II) ion is combined with flavin in acetone, the resulting combination gives absorption maxima at 475 and 380 nm.[4]

The second proposition of the Selbin paper is that the species $Mo^{IV}OCl_3^-$ is produced by hydrolysis (which, for the synthetic conditions, requires that the chloroform solvent contain 0.06 *M* H_2O)

$$Mo^{IV}Cl_4 + H_2O \rightarrow Mo^{IV}OCl_3^- + HCl + H^+ \qquad (1)$$

and is stable in the presence of protonated flavin. The infrared, uv–visible, and ESR data of the paper do not support this conclusion. Haight[5] has shown that Mo(V) ions dimerize to $Mo^V{}_2O_3Cl_8{}^{4-}$ in 1–5 *F* HCl to give a diamagnetic species with absorption maxima at 710, 450, and 310 nm. This species, as $(Et_4N^+)_4(Mo^V{}_2O_3Cl_8{}^{4-})$, has been studied by infrared analysis (in KBr)[6] and exhibits a strong band due to Mo=O at 983 cm^{-1} (as well as weaker bands at 958, 735, and 516 cm^{-1}). This frequency is identical with that for the purported $(HFl^+)(Mo^{IV}OCl_3^-)$ complexes. Mitchell[7] has studied the $Mo^V{}_2O_3Cl_4(bipy)_2$ complex by infrared and uv–visible spectroscopy and observed a strong Mo=O infrared band at 966 cm^{-1} and λ_{max} at 704, 513, and 413 nm. Similarly, for $Mo^V{}_2O_3(NCS)_8{}^{4-}$ there is a Mo=O band[8] at 950 cm^{-1} and λ_{max} at 813 and 529 nm, and for $Mo^V{}_2O_3(oxine)_4$ there is a Mo=O band at 940 cm^{-1} and λ_{max} at 540 and 400 nm. All of these oxo-bridged Mo(V) complexes $(Mo^V{}_2O_3L_nX_m)$ are dark red or dark purple, as are the compounds in the Selbin paper (λ_{max} at 509–525 nm). In contrast, previously reported[9-11] $Mo^{IV}O(oxine)_2$ and $Mo^{IV}OX_2L_2$ compounds are light pink, lilac, light green, or light blue, with an infrared band at 930–950 cm^{-1}. The molybdenum(IV)–oxine complex exhibits weak uv–visible absorption bands at 689, 585, and 524 nm. The reported absence of infrared bands due to Mo–O–Mo in the Selbin compounds may result because they are obscured by flavin bands or are too weak to observe.

On the basis of electrochemical data in aprotic solvents,[1] reaction 1 almost certainly would be followed by an oxidation of the Mo(IV) species by either air or protons (under acidic conditions)

$$4Mo^{IV}OCl_3^- + O_2 + 4H^+ \rightarrow 4Mo^VOCl_3 + 2H_2O \qquad (2a)$$

$$Mo^{IV}OCl_3^- + H^+ \rightarrow Mo^VOCl_3 + {}^1/{}_2H_2 \qquad (2b)$$

and then a dimerization reaction, analogous to that of Haight,[5] to give a dark red or dark purple diamagnetic species

$$2Mo^VOCl_3 + H_2O \rightarrow Mo^V{}_2O_3Cl_6{}^{2-} + 2H^+ \qquad (3)$$

Hence, the probable overall reaction is either

$$4Mo^{IV}Cl_4 + O_2 + 4H_2O \rightarrow 2Mo^V{}_2O_3Cl_6{}^{2-} + 4HCl + 4H^+ \qquad (4a)$$

or

$$2Mo^{IV}Cl_4 + 3H_2O \rightarrow Mo^V{}_2O_3Cl_6{}^{2-} + H_2 + 2HCl + 2H^+ \qquad (4b)$$

In turn, the excess protons would protonate the flavin molecules

$$Fl + H^+ \rightarrow HFl^+ \qquad (5)$$

and lead to the formation of an ionic salt or adduct

$$2HFl^+ + Mo^V{}_2O_3Cl_6{}^{2-} \rightarrow (HFl^+)_2(Mo^V{}_2O_3Cl_6{}^{2-}) \qquad (6)$$

Previous work[12] has established that the major uv–visible absorption bands for protonated flavins (HFl^+) occur at λ_{max} 390, 262, and 200 nm, while the neutral flavin species (Fl) has bands at λ_{max} 450, 350–370, 270, and 218–230 nm. The data in the Selbin article for the neutral flavin models have bands at λ_{max} 440, 330–350, and 265–270 nm. For their isolated molybdenum–flavin compounds the absorption bands were observed at λ_{max} 375–417 and 303–310 nm; in contrast, the tetraacetate derivative of riboflavin in combination with $MoCl_4$ gave a product with λ_{max} at 450 and 350 nm (which are analogous to the bands for neutral flavins[12]).

The change in the frequencies for the flavin infrared bands with the addition of $MoCl_4$ that is observed by the Selbin group can be rationalized equally well as being the result of protonation of N(5) in HFl^+, rather than N(1). This would cause the C=O(2) frequency to increase and the C=O(4) frequency to decrease and would give the observed N—H band. The NMR data of Table III in the Selbin paper also are indicative of N(5) protonation.

The conclusion that the actual isolated species really are salts or adducts with the formula $[(HFl^+)_2(Mo^V{}_2O_3Cl_6{}^{2-})]$ is supported by the elemental analysis data of Table I in the Selbin paper. Recalculation of the elemental content on the basis of this formula gives values that overall are in closer agreement with the experimental values, especially in the case of molybdenum, chlorine, and nitrogen.

To test the proposition that $Mo^{IV}Cl_4$ is oxidized to Mo(V) and dimerized under the conditions of the Selbin studies, we added Mo^VOCl_3 to acetonitrile and recorded the uv–visible spectrum for the solution; λ_{max} are observed at 700, 463, and 363 nm. In a second experiment $Mo^{IV}Cl_4$ was added to acetonitrile to give a solution with λ_{max} at 700, 500, and 402 nm.[13] These data are analogous to those for $Mo^V{}_2O_3Cl_n$ complexes[5] and indicate that $Mo^{IV}Cl_4$ is hydrolyzed by residual water, oxidized by the resultant protons and/or oxygen, and