(24) The salt crystallizes in the chiral space group $P6_3$ but Strandberg[21] did not record whether he determined the absolute configuration of the anion in the crystal he studied.

(25) The three trans Mo(IV) complexes $MoO_2(CN)_4^{4-}$, $MoO(OH)(CN)_4^{3-}$, and $MoO(OH_2)(CN)_4^{2-}$ illustrate the principle involved. Protonation of one oxygen increases the Mo–O(–H) bond length and shortens the bond to the trans oxygen, thereby decreasing the basicity of the latter. Consequently the second proton becomes bound to the hydroxo oxygen: P. R. Robinson et al., *Inorg. Chem.*, **14**, 2035 (1975). The structure of $PMo_9O_{34}H_6^{3-}$ is such that similar bond length changes can be transmitted through several metal atoms.

(26) Starting at one of the "equatorial" oxygen atoms the sequence of Mo–O bond lengths is 2.12, 1.78, 2.07, 1.83, 2.03, 1.77, 2.14, 1.75, 2.12, 1.78, 2.06, 1.84, 2.05, 1.77, 2.14, and 1.76 Å. There are three such sequences in the whole structure.

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Interpretation of Isosbestic Points

AIC50883X

Sir:

The significance of the existence, or lack thereof, of an isosbestic point in systems containing three or more absorbing species is deceptively complex. In a recent article[1] incorrect criteria were offered for recognizing systems in which an isosbestic point exists. [We ignore the possibility of accidental occurrence of isosbestic points due to fortuitous combinations of extinction coefficients at some wavelength. A consideration of this problem, conditions under which it occurs, and a method for determining if the isosbestic point is accidental by the method of forming ξ curves from the sum of spectral lines with shifted wavelength axes have been discussed by Kwiatkowski.[5]] The stated criteria for the existence of an isosbestic point are that "2 + N species may be present providing there are N relations between the concentrations of these species and these relations are independent of the parameter being varied". A series of consecutive equilibria

$$A + B \rightarrow AB \tag{1}$$

$$AB + B \rightarrow AB_2 \tag{2}$$

provides the classic example in which the lack of an isosbestic point is used to infer[2] the simultaneous existence of more than two absorbing species, A, AB, and AB_2. Yet this system satisfies the above criteria offered[1] for the existence of an isosbestic point. In this system, there are three absorbing species, so we need find only one relation ($N = 1$) which is independent of B. This relation is given by the ratio of the two equilibrium constants for eq 1 and 2

$$K_1/K_2 = [AB]^2/[A][AB_2] \tag{3}$$

Clearly, the above criteria would predict an isosbestic point in this classic example where one is not obtained.

Another example of the failure of the Stynes criteria[1] is a system in which two different acids A and A′ are competing for a single base B

$$A + B \rightarrow AB \tag{4}$$

$$A' + B \rightarrow A'B \tag{5}$$

The four absorbing species are A, A′, AB, and A′B. A series of solutions is investigated in which the initial concentrations of A and A′ are held constant and B is varied. With four absorbing species, N equals 2 and the two relationships independent of the quantity being varied, B, are

$$[A'] + [A'B] = k'$$

$$[A] + [AB] = k \tag{6}$$

An isosbestic point will not result as B is varied even though there are two "relationships between the absorbing species".[1]

A correct set of criteria for the existence of an isosbestic point can be best illustrated by considering an ambidentate donor, the system treated by Stynes.[1] For example, if a basic molecule containing nitrogen and oxygen donor atoms were able to coordinate to an acid, A, to produce either an oxygen-bound complex or a nitrogen-bound complex, the mixture of complexes AN (nitrogen bound), AO (oxygen bound), and free A (an absorbing Lewis acid) would give rise to an isosbestic point. The absorbance (A) for such a system is given by

$$A = \epsilon_A[A] + \epsilon_N[AN] + \epsilon_O[AO] \tag{7}$$

The equilibrium constant expressions are given by

$$K_O = [AO]/[A][B]$$

$$K_N = [AN]/[A][B]$$

$$K_O + K_N = \frac{[AO] + [AN]}{[A][B]} = \frac{[AB]}{[A][B]} \tag{8}$$

where we define [AO] + [AN] = [AB]. The fraction of complex, X_O, which is oxygen coordinated, is given by

$$X_O = \frac{K_O}{K_O + K_N} = \frac{[AO]/[A][B]}{[AB]/[A][B]} = \frac{[AO]}{[AB]} \tag{9}$$

The fraction which is nitrogen coordinated is similarly derived to be

$$X_N = [AN]/[AB] \tag{10}$$

Now the total absorbance becomes

$$A = \epsilon_A[A] + \epsilon_O X_O[AB] + \epsilon_N X_N[AB]$$

or

$$A = \epsilon_A[A] + (\epsilon_O X_O + \epsilon_N X_N)[AB] = \epsilon_A[A] + \epsilon'[AB] \tag{11}$$

Since the sum of [A] and [AB] is a constant and there must be a place in overlapping spectra where $\epsilon_A = \epsilon'$, an isosbestic point will be obtained even though three absorbing species exist.

We have taken two absorbing species whose ratio is a constant independent of the parameter being varied and translated them to what is effectively a single absorbing species via eq 11. The general criteria thus are that 2 + N absorbing species will give rise to an isosbestic point if there are N *independent* equations of the form

$$[Y]/[Z] = k$$

where Y and Z are two of the absorbing species in the system and the value of k is independent of the parameter being varied.

As an example of the application of these criteria, consider an acid which can form two isomers with a base AB and A*B—e.g., $Cu(hfac)_2$[3] which forms basal and apical adducts—forming an adduct with a base that can form two isomers with an acid AB and AB*—e.g., N-methylimidazole[4] bound through the amine and imine nitrogen. Five absorbing species (A, AB, A*B, AB*, A*B*) can exist

$$A + B \rightarrow AB$$

$$A + B \rightarrow A^*B$$

$$A + B \rightarrow AB^*$$

$$A + B \rightarrow A^*B^*$$

so three constants are needed. The equilibrium constants are

$$K_1 = [AB]/[A][B]$$

$$K_2 = [A^*B]/[A][B]$$

$$K_3 = [AB^*]/[A][B]$$

$$K_4 = [A^*B^*]/[A][B]$$

We now note that three independent ratios exist which are independent of B

$$K_1/K_2 = [AB]/[A^*B]$$

$$K_2/K_3 = [A^*B]/[AB^*]$$

$$K_3/K_4 = [AB^*]/[A^*B^*]$$

Therefore, an isosbestic point is expected. Any other ratio of equilibrium constants, e.g., K_1/K_3, is not independent of the three ratios written. If we do not obtain an isosbestic point in a system that could potentially be described this way, these criteria are not being met.

If one applies these criteria to those systems in which the Stynes criteria would incorrectly predict the existence of an isosbestic point, our criteria do not predict the existence of an isosbestic point. The general rules presented here apply to a large number of systems. However, rote application of rules is no substitute for an understanding of the systems under consideration.

References and Notes

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Evidence for Ortho Metalation of Coordinated Triphenyl Phosphite Using Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy

AIC60036+

Sir:

Recent work from these laboratories[2] has demonstrated the ability of ^{31}P NMR spectroscopy to discriminate between metalated and unmetalated triphenyl phosphite ligands in the cyclopentadienyliron complexes **1**–**3** (Table I). Ortho metalation of coordinated triphenyl phosphite was found to be accompanied by a large downfield ^{31}P chemical shift (ca. 30–35 ppm) relative to the unmetalated coordinated ligand.[2] This observation appears to be a specific example of a more general phenomenon since it is now well documented that phosphorus in *five-membered* chelate rings shows a large downfield ^{31}P chemical shift relative to phosphorus in analogous monodentate coordinated ligands.[3–10]

In an effort to expand upon our earlier observations,[2] we have investigated the known[11–13] series of manganese complexes **4**–**7** using ^{31}P NMR spectroscopy.[14] We have also compiled from the literature the limited amount of ^{31}P NMR data available for related ortho-metalated complexes. Relevant ^{31}P NMR data are tabulated in Table I.

Garrou[10] has recently defined a useful parameter, Δ_R, which reflects the chelate "ring contribution" to the ^{31}P chemical shift of a phosphorus atom in a metal-coordinated chelate ligand. In the case of the ortho-metalated triphenyl phosphite ligand Δ_R can be expressed as $\Delta_R = \delta_{met} - \delta_{unmet}$, where δ_{met} and δ_{unmet} are the ^{31}P chemical shifts of metalated and unmetalated phosphite ligands, respectively, in equivalent stereochemical environments. An *internal* Δ_R value will be defined as one derived using δ_{met} and δ_{unmet} parameters from the *same* complex. An *external* Δ_R value corresponds to one derived using δ_{met} and δ_{unmet} parameters from *closely related* complexes.

Manganese Complexes. Geometries of the complexes **4**–**7** have been established as those indicated by infrared spectroscopy in the CO stretching region.[11–13,16] The ^{31}P chemical shifts of the iron complexes **1**–**3** are observed at lower field relative to the corresponding manganese analogues **4**, **6**, and **7**, respectively. This is interpreted in terms of the better electron-withdrawing ability of the $Mn(CO)_3$ group vs. the isoelectronic $Fe(\eta^5\text{-}C_5H_5)$ group.[17]

A comparison of the ^{31}P chemical shifts of **4** and **5** indicates that substitution of the CO group trans to $P(OPh)_3$ in **4** with a second phosphite ligand results in a small downfield shift (4 ppm). This change is in accord with ^{31}P NMR data on related octahedral-like systems in which the ^{31}P chemical shift of a coordinated phosphorus ligand is dependent on the nature of the trans ligand.[18–20] For example, the ^{31}P chemical shifts[18] of $W(CO)_5P(OPh)_3$ (−130.3 ppm) and *trans*-$W(CO)_4[P(OPh)_3]_2$ (−132.3 ppm) exhibit the same trend noted for **4** and **5**.

In contrast to CO substitution in **4**, ortho metalation of coordinated $P(OPh)_3$ (**4** → **6**) results in a substantial change in ^{31}P chemical shift. Thus, the external Δ_R value derived from the related complexes **4** and **6** is −33.4 ppm. A comparable Δ_R value (−31.1 ppm) was earlier observed from **1** and **2**, the $Fe(\eta^5\text{-}C_5H_5)$ analogues of **4** and **6**, respectively.[2]

The ^{31}P NMR spectrum of **7** consists of two doublets of equal intensity with $^2J_{PP} = 107$ Hz. Distinction between metalated (−193.8 ppm) and unmetalated (−157.1 ppm) ligands is unambiguous by comparison with **4**–**6**. The internal Δ_R value of −36.7 ppm in **7** compares quite favorably with the external Δ_R value obtained above. An internal Δ_R value of −33.6 ppm is obtained from the isoelectronic complex **3**.[2] The slightly more positive chemical shift of the $P(OPh)_3$ group in **7** compared to **4** and **5** is consistent with the mutual cis orientation of the two phosphorus atoms in the former compound. A similar trend is noted in related octahedral-like complexes containing cis $P(OPh)_3$ groups.[18] In contrast, the resonance of the ortho-metalated ligand is scarcely shifted from its value in **6**.

The ^{31}P NMR data on the manganese series **4**–**7** thus display the same internal consistency and trends noted previously[2] for the iron series **1**–**3**. In particular, these data further illustrate the dramatic difference in ^{31}P chemical shifts of metalated and unmetalated phosphite ligands having strictly comparable stereochemical environments.

Other Complexes. Our interpretation of the ^{31}P NMR spectrum[21] of **8** has been dealt with previously[2] and will not be further discussed here. Two internal Δ_R values can be obtained for this complex depending upon the choice of unmetalated ligand as reference. As seen in Table I, however, the Δ_R values are not appreciably different.

Work by Robinson and co-workers[22] has provided ^{31}P NMR data on several six-coordinate osmium complexes containing