Intramolecular Rearrangements in Neutral ML₅ Species

Sir:

Nuclear resonance studies of neutral molecules of the form ML_5 have played an important role in the development of concepts of stereochemical nonrigidity. PF_5 was studied at an early date[1] and $Fe(CO)_5$ has been examined by a number of workers.[2,3] All studies of this type failed to reveal the inequivalences in the NMR spectra expected for a trigonal bipyramidal or square pyramidal geometry. More recently a number of cationic group 8 phosphite complexes have been shown to have D_{3h} symmetry in solution.[4] Although a dominant role for ion pairing in the rearrangement process appears unlikely, the corresponding analysis for a neutral complex provides an important step in the study of ML_5 rearrangements.

The neutral complex $Fe[P(OCH_3)_3]_5$ has recently been reported by Muetterties and Rathke[5] and is described as having D_{3h} stereochemistry in solution. We have prepared this complex by sodium amalgam reduction of $FeBr_2$ in the presence of excess phosphite, purifying the final product by chromatography.

Complexes of the higher alkyl phosphites are less accessible. The new complex $Fe[P(OC_2H_5)_3]_5$ can be obtained by Na:Hg reduction of $FeBr_2$ in THF in the presence of excess $P(OC_2H_5)_3$ at low temperatures. The compound is isolated as a yellow crystalline product by chromatography followed by low temperature crystallization. Yields of 40% {Fe[P-$(OCH_3)_3]_5$} and 50% {Fe[P(OC₂H₅)₃]₅} were obtained; both complexes decompose in solution above ~80° but are stable up to ~150° in the solid for short periods of time. $Fe[P(O-n-C_3H_7)_3]_5$ was obtained by Na:K alloy reduction; this was an in situ preparation and the product was not isolated.

Figure 1 shows the observed and calculated low temperature limit A_2B_3 ³¹P{¹H} spectra for $Fe[P(OC_2H_5)_3]_5$ (J_{AB} = 144.5 Hz, δ_{AB} 7.5 ppm) at −105° and for Fe[P(O-n-$C_3H_7)_3]_5$ (J_{AB} = 144 Hz, δ_{AB} 6.7 ppm) at −95°. The observed and calculated spectra for $Fe[P(OCH_3)_3]_5$, as a function of temperature, are shown in Figure 2 and give the activation parameters $\Delta G^{\ddagger}_{200}$ = 8.8 kcal mol⁻¹, $\Delta H^{\ddagger}_{200}$ = 8.6 kcal mol⁻¹, and $\Delta S^{\ddagger}$ = −1.5 cal mole⁻¹ deg⁻¹. The $\Delta G^{\ddagger}_{200}$ value is to be compared with the estimated values of ~10 and ~8 kcal mol⁻¹ for $Co[P(OCH_3)_3]_5^+$ and Ni-$[P(OCH_3)_3]_5^{2+}$, respectively.[4] The trend indicates a maximum at Co for the stability of the D_{3h} ground state with respect to the C_{4v} transition state.

A comparison of the observed spectrum of Fe[P-$(OCH_3)_3]_5$ near the slow exchange limit with spectra calculated for the two possible types of permutational behavior in the rearrangement process is shown in Figure 3 at −104°. As with the cationic species,[4] behavior of type A (simultaneous exchange of two equatorial with the two axial lig-
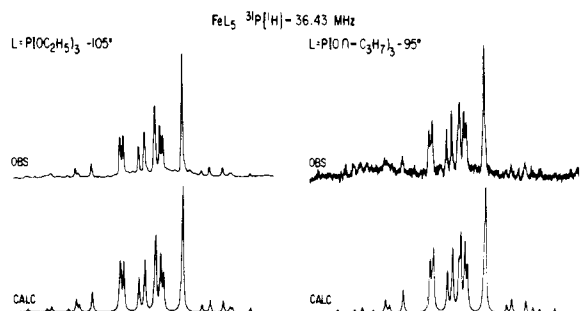

Figure 2. Observed and calculated ³¹P{¹H} spectra for $Fe[P(OCH_3)_3]_5$ as a function of temperature using an A_2B_3 model with simultaneous exchange of two equatorial with the two axial ligands.
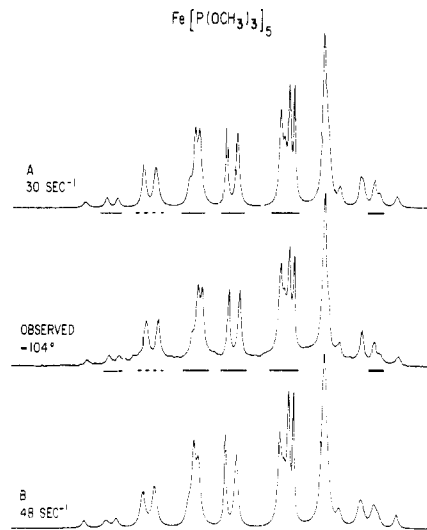
Figure 3. Comparison of ³¹P{¹H} spectrum of $Fe[P(OCH_3)_3]_5$ near the slow exchange limit, with spectra simulated using type A and type B exchange. See text. (It should be pointed out that confident assignment of A type exchange requires careful comparison of observed and calculated spectra over a range of temperatures; in this figure the features underlined with solid lines support type A exchange, and those underlined with dotted lines are perhaps ambiguous.)

ands) gives a better fit at this, and other temperatures, than does behavior of type B (sequential exchange). The results are consistent with a Berry rearrangement[6] mechanism having a C_{4v} transition state as was assumed in the earlier discussion.

There is an increase in the barrier to rearrangement with increasing length of the alkyl side chain supporting the suggestion that steric crowding in the transition state is important in determining the barrier height. The free energy of activation $\Delta G^{\ddagger}_{246}$ for $Fe[P(OC_2H_5)_3]_5$ is 11.2 kcal mol⁻¹. The chemical shift separations of the two types of phosphorus are strongly temperature dependent, indicating that the effect is due to varying populations of different conformers[4] and ruling out the possibility, present in the cationic study,[4] that it is due to ion pairing.

Figure 1. Observed and calculated slow exchange limits ³¹P{¹H} NMR spectra for solutions of $Fe[P(OC_2H_5)_3]_5$ and $Fe[P(O-n-C_3H_7)_3]_5$ in n-pentane.
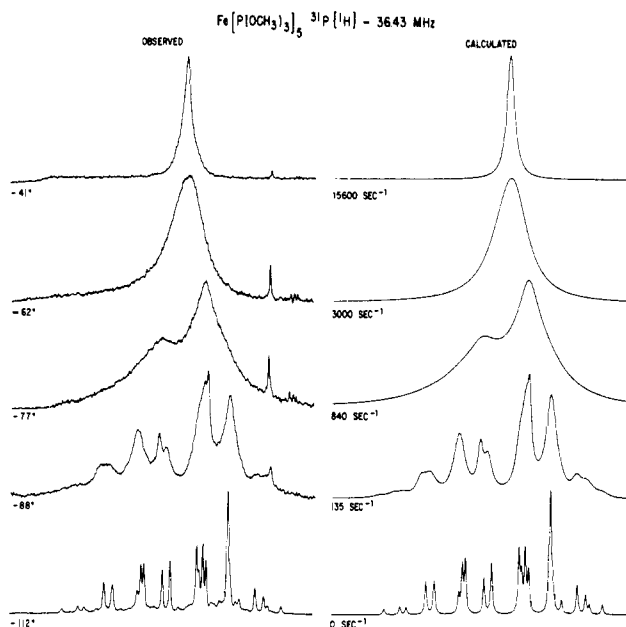
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Molybdenum in Oxidation State 2.5+ in Aqueous Solution

Sir:

We wish to report the existence of a stable molybdenum species in the 2.5+ oxidation state in aqueous solution.

Cotton, Frenz, and Webb[1] observed that when $K_4Mo_2(SO_4)_4\cdot2H_2O$ (compound I) was recrystallized by allowing its solution to mix by diffusion, through a glass frit, with a saturated solution of K_2SO_4, a mixture of two different crystals was obtained: pink crystals of the parent compound I and red-blue crystals of a new compound II, which was shown by X-ray structure analysis to be $K_3Mo_2(SO_4)_4\cdot3.5H_2O$ and to have a bond of order 3.5 between the Mo atoms. A similar compound derived from an ethylene diammine complex of Mo(II) was recently prepared by Bowen and Taube.[2] The oxidation state of molybdenum in these compounds is 2.5+.

In the course of this study it became necessary to prepare compound II in a pure state, i.e., free from admixture with I. The mode of preparation is given at the end of this communication.

When the pure compound II was dissolved in oxygen free H_2SO_4 (2 N) a blue solution was obtained. The solid II may be recovered from the solution by the addition of a saturated K_2SO_4 solution. This solution could be oxidized by air to Mo(IV)[3] but was stable in oxygen-free solutions of this acid. The spectrum of this blue solution had maxima at 412 nm (ϵ = 16.9) and 573 nm (ϵ = 17.5) (Figure 1) and was similar to the reflectance spectrum of II (with maxima at 410 and at 573 nm).

The oxidation state of molybdenum in this solution was derived from the ratio of the permanganate titer of an aliquot (after discharging into excess Fe(III)) to the permanganate titer of the total molybdenum analysis (carried out on an air-oxidized aliquot after it was reduced to Mo(III) by a Jones Reductor and discharged into excess Fe(III)).[4] The ratio found was 1.17 ± 0.01 and corresponded to an oxidation number of 2.5+. The same result was obtained when a weighed sample of solid II was dissolved directly in a ferric salt solution and its permanganate titer compared to that of its total Mo analysis.

The identity of the oxidation state and the similarity of the spectra of solid II and the blue solution support the conclusion that the solution contains a molybdenum species of oxidation number 2.5+ in which the fundamental unit Mo_2^{5+} of II, with its Mo-to-Mo bond of order 3.5 is preserved.
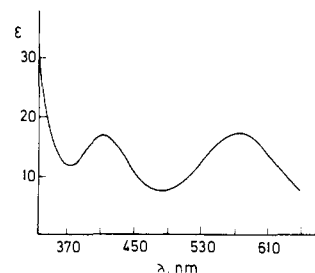

Figure 1. Absorption spectrum of Mo_2^{5+} in H_2SO_4 (2 N).

The blue solution of Mo 2.5+ was reduced to a red solution of Mo_2^{4+} [2,6] by a Jones reductor. Reduction of Mo_2^{5+} to Mo_2^{4+} would involve the transfer of one electron from the reducing agent to the half-filled δ molecular orbital of the 3.5 order bond.[1]

The stability of Mo 2.5+ in sulfuric acid solutions is in marked contrast to its instability in other strong acids. When II was dissolved in aqueous HCl or p-toluenesulfonic acid (HPTS) the pale blue color observed initially turned into a deep red color. This red solution passed unchanged through a Jones reductor, thereby ruling out the possibility that the color was due to Mo(IV)[3] or any other species of higher oxidation number (all of which would be reduced to the green binuclear Mo(III) ion[5]).

A typical absorption band of Mo_2^{4+} at 514 nm[2,6] appeared within minutes in a freshly prepared solution of II in HPTS and its intensity increased with time. The conclusion that Mo_2^{4+} was formed spontaneously in these solutions was confirmed by the chromatographic behavior of the red species on both cation and anion exchange columns, which was characteristic[6] for Mo_2^{4+}. A typical deep blue color which appears immediately upon addition of KCNS to Mo_2^{4+} was also observed upon addition of this reagent to the red solution.

The average oxidation number of Mo in the solution of II in HPTS did not change after it had turned red, and remained 2.5+; therefore it was evident that the blue molybdenum 2.5+ species underwent disproportionation in this solution. The disproportionation reaction may be reversed by the addition of a saturated solution of K_2SO_4; the red color disappears and solid II is precipitated.

While Mo(II) was established as the reduced product of the disproportionation reaction, the nature of the oxidized product could not be determined unequivocally. The decomposed solution of II in HPTS was absorbed on a cation exchange column, after removal of Mo(II). A band of a 3+ ion similar to $Mo(H_2O)_6^{3+}$ [2,6] was observed, but could not be eluted in sufficient purity to allow positive spectral identification.[2,7] A Mo(IV) band[3] was observed on the column and identified after elution, but one may not conclude that it was necessarily a primary product of the disproportionation reaction. Mo(IV) might have been formed by a secondary reaction such as the oxidation of $Mo(H_2O)_6^{3+}$ by water.[3]

The fact that Mo 2.5+ is stable only in the presence of sulfate supports the conclusion that it exists in solution as a sulfato complex related to II, such as the $Mo_2(SO_4)_4^{3-}$ ion or a partly aquated sulfato complex. The reversal of the disproportionation reaction by K_2SO_4 indicates that this stabilization of Mo 2.5+ by sulfate is of thermodynamic rather than of kinetic origin.

Work is in progress in this laboratory on the kinetics of the disproportionation reaction and the identification of the oxidation products.

In the preparation of $K_3Mo_2(SO_4)_4\cdot3.5H_2O$, a saturated solution of $K_4Mo_2(SO_4)_4\cdot2H_2O$ in H_2SO_4 (2 N) was oxi-