Ph_3AsMe^+TCNQ,[48] and $(Cs^+)_2(TCNQ)_3^{2-}$ [49] occur at fields equal to or greater than that observed for the free electron and exhibit derivative peak to peak line width <5 Oe.[47,49]

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Stereochemical Rigidity in ML_5 Complexes. 4. Preparations and Nuclear Magnetic Resonance Line-Shape Analyses of Intramolecular Exchange in Neutral ML_5 Complexes of Iron, Ruthenium, and Osmium

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Abstract: A series of zerovalent d^8 ML_5 complexes has been synthesized (M = Fe, Ru, Os; L = phosphite). These novel species are characterized and their intramolecular exchange behavior is established by $^{31}P\{^1H\}$ NMR and a complete line-shape analysis. The intramolecular rearrangement barriers fall in the range of 7-9 kcal/mol. The variation of the rearrangement barrier as a function of the metal for the entire d^8 ML_5 series is defined by the present study and our previous work. The exchange processes and rearrangement barrier ordering are consistent with previous results for the cationic ML_5 species; therefore, the possibility of a dominant role for ion pairing in the previous studies is excluded.

Since the original work of Cotton and co-workers[1a] showing stereochemical nonrigidity in $Fe(CO)_5$, there has been considerable interest in defining the factors which influence barriers to intramolecular exchange in five-coordinate complexes. We have previously made extensive solution studies[2-6] of cationic d^8 ML_5 complexes; more recently we have turned our attention to the unknown zerovalent d^8 ML_5 species, where L is an alkyl phosphite. The $M(PF_3)_5$ complexes (M = Fe, Ru, Os) had been reported earlier by Kruck and Prasch.[7] While our work was in progress, Muetterties and Rathke independently reported the preparation of $Fe[P(OCH_3)_3]_5$ by sodium amalgam reduction.[8] We have described an NMR study of this complex in a communication,[9] and now wish to report the preparation and NMR behavior of the previously unknown $Ru[P(OCH_3)_3]_5$ and $Os[P(OCH_3)_3]_5$ complexes. We have also prepared $Fe[P(OC_2H_5)_3]_5$ and $Fe[P(O\text{-}n\text{-}C_3H_7)_3]_5$. This work permits a comparison of rearrangement barriers for the complete series of nine d^8 $M[P(OCH_3)_3]_5$ complexes, establishes a trigonal bipyramidal stereochemistry in all cases (from A_2B_3 patterns in the $^{31}P\{^1H\}$ NMR spectra), and confirms that ion pairing does not have a dominant role in the rearrangement process.

A detailed line-shape analysis of $Fe[P(OCH_3)_3]_5$ shows that there is simultaneous exchange of the pair of axial with a pair of equatorial ligands in the rearrangement process. This is the same permutation found in the cationic d^8 ML_5 species and is consistent with the Berry mechanism. The barriers to rearrangement vary from 7 to 9 kcal/mol for the three metals where the ligand is $P(OCH_3)_3$; the ordering is Fe > Ru < Os. This ordering is in agreement with previous results[5] on the isoelectronic cationic species. Intermolecular exchange does not occur for these complexes at an accessible temperature.

Results

A. Iron. The low-temperature limiting spectra have been obtained for three FeL_5 complexes. The complexes all have A_2B_3 patterns in the $^{31}P\{^1H\}$ NMR, indicating that the molecules have D_{3h} symmetry on the NMR time scale. The temperature-dependent spectra for two of the complexes have been analyzed and their rearrangement barriers calculated.

(i) **$Fe[P(OCH_3)_3]_5$.** This complex was prepared by sodium amalgam reduction of $FeBr_2$ in the presence of excess phosphite in a tetrahydrofuran solution. The product was purified by chromatography and the NMR data were obtained using pentane as the solvent.

The low-temperature limiting spectrum is obtained at −122 °C and is characteristic of a tightly coupled A_2B_3 spin system. The relevant NMR parameters are given in Table I.

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 1 at −104 °C. As with the cationic species,[5] behavior of type A (simultaneous exchange of two equatorial with the two axial ligands) 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[10] mechanism having a C_{4v} transition state.

Evidence for intermolecular exchange on the NMR time scale was sought using a solution of $Fe[P(OCH_3)_3]_5$ and $P(OCH_3)_3$ in benzonitrile. At temperatures of up to 140 °C no intermolecular exchange was apparent; the complex is stable for only a few minutes at this temperature.

(ii) **$Fe[P(OC_2H_5)_3]_5$.** This complex was prepared by a method

Table I. $^{31}P\{^1H\}$ Chemical Shifts and Coupling Constants for ML_5 Complexes at the Temperature Noted

Complex	δ_A,[a] ppm	δ_B, ppm	J_{AB}, Hz	Temp
$Fe[P(OCH_3)_3]_5$	−187.8	−176.4	145	−104
$Fe[P(OC_2H_5)_3]_5$	−180.9	−171.1	144.5	−105
$Ru[P(OCH_3)_3]_5$	−155.6	−179.7	77.5	−137
$Os[P(OCH_3)_3]_5$	−111.0	−145.2	61	−130

[a] $\delta < 0$ means downfield from 85% H_3PO_4.

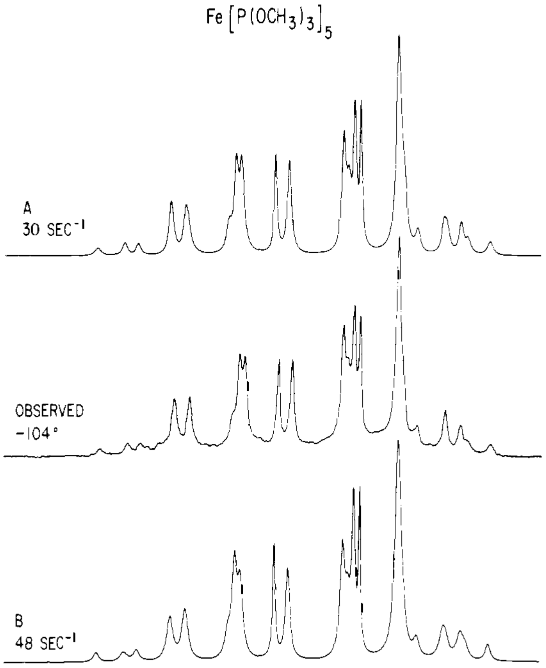

Figure 1. Comparison of $^{31}P\{^1H\}$ spectrum of $Fe[P(OCH_3)_3]_5$ near the slow-exchange limit, with spectra simulated using type A and type B exchange (see text). (It should be pointed out that confident assignment of A-type exchange requires careful comparison of observed and calculated spectra over a range of temperatures).

analogous to that for the trimethyl phosphite complex. The low-temperature (−105 °C) limiting $^{31}P\{^1H\}$ spectrum in pentane is a tightly coupled A_2B_3 spin system. Relevant NMR parameters are given in Table I and thermodynamic parameters derived from a line-shape analysis of the NMR spectra are given in Table II.

Figure 2 shows the observed and calculated $^{31}P\{^1H\}$ spectra for $Fe[P(OC_2H_5)_3]_5$ as a function of temperature (exchange rate). The calculated spectra use an A_2B_3 model assuming simultaneous exchange of two axial ligands with two equatorial ligands. The chemical shift difference between the A and B sites is somewhat temperature dependent. From an Arrhenius plot the rate expression

$$\text{rate} = 10^{11.5}e^{-10\,200/RT}\ \text{s}^{-1}$$

is found and the thermodynamic parameters given in Table II are calculated.

The $\Delta G^{\ddagger}_{200}$ values for $Fe[P(OCH_3)_3]_5$ (8.8 kcal/mol) and $Fe[P(OC_2H_5)_3]_5$ (10.8 kcal/mol) once again establish that there is an increase in the rearrangement barrier with increasing length of the alkyl side chain. This supports the suggestion that steric crowding in the transition state is important in determining the barrier height.

(iii) **$Fe[P(OC_3H_7)_3]_5$.** This complex was prepared via a NaK alloy reduction of $FeBr_2$ in the presence of excess phosphite in tetrahydrofuran. The complex was not isolated for further characterization, since the reduction gives only a fairly low yield. Only a low-temperature (−95 °C) limit $^{31}P\{^1H\}$ spectrum in pentane was recorded. NMR parameters are given in Table I.

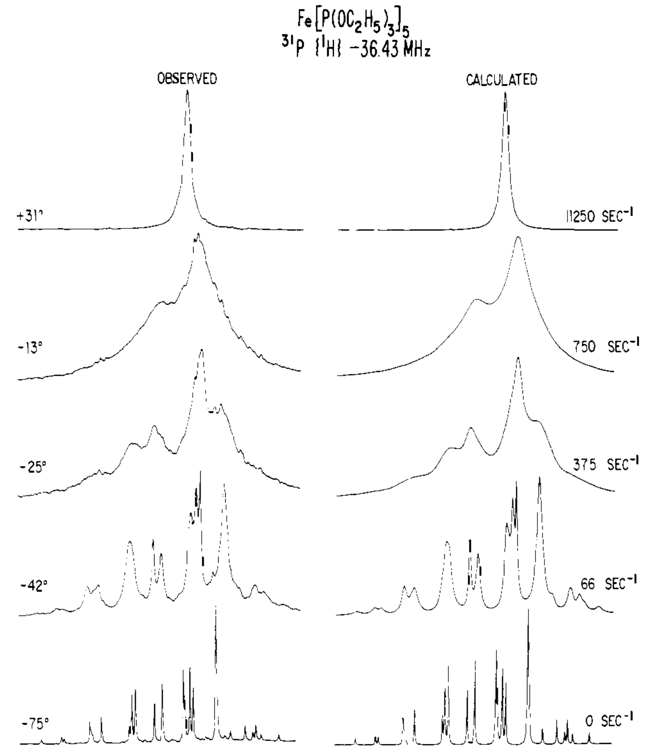

Figure 2. Observed and calculated $^{31}P\{^1H\}$ spectra for $Fe[P(OC_2H_5)_3]_5$ as a function of temperature using an A_2B_3 model with simultaneous exchange of two equatorial with the two axial ligands.

B. Ruthenium. $Ru[P(OCH_3)_3]_5$ has been prepared by a sodium amalgam reduction of $RuCl_2[P(OCH_3)_3]_4$ in the presence of excess phosphite in a tetrahydrofuran solution. The product, purified by chromatography, is identified by its low-temperature (−125 °C) limit A_2B_3 $^{31}P\{^1H\}$ NMR spectrum.

Variable-temperature $^{31}P\{^1H\}$ spectra were recorded in a solution of toluene-d_8 and chlorodifluoromethane. The chemical shift difference (δ_{AB}) is quite a strong nonlinear function of the temperature; therefore the exchange rates obtained from the line-shape analysis are somewhat less accurate than usual. The resulting thermodynamic parameters (Table II) are also somewhat less accurate (the error in $\Delta G^{\ddagger}$ is ±0.3 kcal/mol instead of the usual ±0.2 kcal/mol). NMR parameters for the slow exchange limit spectrum are given in Table I.

The observed and calculated DNMR spectra are shown in Figure 3. The calculated spectra assume a simultaneous exchange of two axial and two equatorial ligands.

Intermolecular exchange was not observable on the NMR time scale in an experiment identical with that done for $Fe[P(OCH_3)_3]_5$.

C. Osmium. $Os[P(OCH_3)_3]_5$ has been prepared by a sodium amalgam reduction of $OsCl_4[P(OCH_3)_3]_2$ in the presence of excess phosphite in a tetrahydrofuran solution. The crude product of this reduction is isolated and used without further purification in the NMR studies.

$Os[P(OCH_3)_3]_5$ in a toluene-d_8/chlorodifluoromethane solution gives the low-temperature (−125 °C) limit A_2B_3 $^{31}P\{^1H\}$ spectrum shown in Figure 4. NMR parameters are given in Table I. Thermodynamic parameters obtained from

Table II. Activation Parameters for Intramolecular Rearrangement in d^8 ML_5 Complexes

Complex	$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol deg)	Temp, K
$Fe[P(OCH_3)_3]_5$	8.8	8.6	−1.5	200
$Fe[P(OC_2H_5)_3]_5$	11.3	9.9	−7.1	200
$Ru[P(OCH_3)_3]_5$	7.2	8.5	6.5	200
$Os[P(OCH_3)_3]_5$	7.6	8.3	3.4	200
$Co[P(OCH_3)_3]_5$	10.[a]			
$Rh[P(OCH_3)_3]_5$	7.5			
$Ir[P(OCH_3)_3]_5$	8.0			
$Ni[P(OCH_3)_3]_5$	8.[a]			
$Pd[P(OCH_3)_3]_5$	6.2			
$Pt[P(OCH_3)_3]_5$	6.5			

[a] Not measured directly; estimated from the corresponding $P(OCH_2)_3CCH_3$ complex.

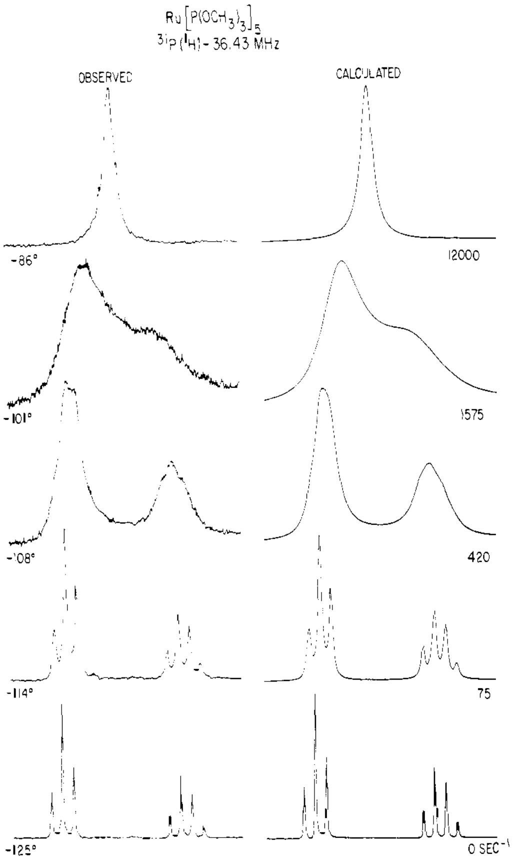

Figure 3. Observed and calculated $^{31}P\{^1H\}$ spectra for $Ru[P(OCH_3)_3]_5$ as a function of temperature using a simultaneous exchange mechanism.

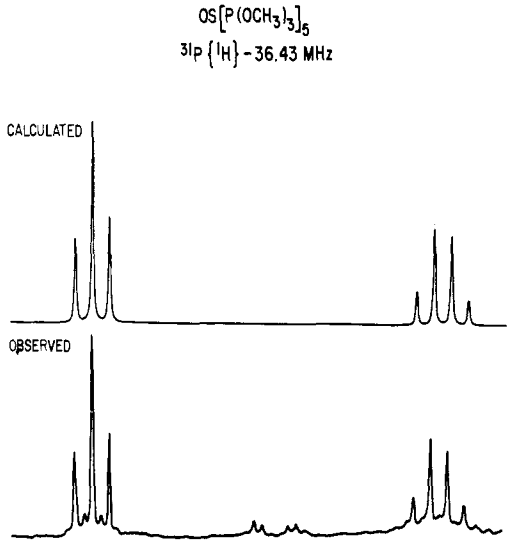

Figure 4. Observed and calculated slow exchange $^{31}P\{^1H\}$ spectra for $Os[P(OCH_3)_3]_5$.

a line-shape analysis (assuming a simultaneous exchange mechanism) are given in Table II.

The presence of impurities in the solution used in this study coupled with the temperature dependence of δ_{AB} make the determination of exchange rates in the line-shape analysis somewhat less accurate than is usual. However the $\Delta G^{\ddagger}{}_{200}$ value of 7.6 kcal/mol is still thought to be accurate within ±0.3 kcal/mol. The calculated rate expression is:

$$\text{Rate} = 10^{13.8}e^{-8700/RT}\ \text{s}^{-1}$$

Conclusions

Stereochemical nonrigidity has been investigated for a series of zerovalent ML_5 complexes where M = Fe, Ru, Os and L is a phosphite ligand. The following points have been demonstrated:

(1) The rearrangement barriers determined in this study when combined with our previous work[11] fully define the variation of the rearrangement barrier with metal for all group 8 d^8 transition metals.

$$\begin{array}{ccccc} \text{Fe} & < & \text{Co} & > & \text{Ni} \\ \vee & & \vee & & \vee \\ \text{Ru} & < & \text{Rh} & > & \text{Pd} \\ \wedge & & \wedge & & \wedge \\ \text{Os} & < & \text{Ir} & > & \text{Pt} \end{array}$$

(2) A dominant role for ion pairing in the rearrangement process is excluded for these zerovalent complexes. The systematic nature of the results for both the zerovalent and cationic species infers that ion pairing does not participate significantly in the rearrangement process for the cationic species.

(3) The chemical shift separation of the axial and equatorial phosphites for these zerovalent species is strongly temperature dependent, an effect which cannot be due to ion pairing. This effect is probably due to varying populations of different conformers.[5]

(4) The $^{31}P\{^1H\}$ NMR studies of the iron complexes again show that the barrier to intramolecular exchange increases with the length of the alkyl side chain.

Experimental Section

$^{31}P\{^1H\}$ Fourier mode NMR spectra (36.43 MHz) were recorded as described in previous publications of this series.[2] All preparations were carried out in the inert atmosphere of a nitrogen drybox using standard procedures. Tetrahydrofuran was distilled under argon from sodium/benzophenone just prior to use. All other solvents were dried over molecular sieves and purged with nitrogen. Reagents were commercially available and used without further purification. Chromatography was done on neutral grade alumina (activity I or II), eluting with pentane.

I. Iron. (A) Pentakis(trimethyl phosphite)iron(0). A 1 l. three-necked flask equipped with mechanical stirrer and nitrogen flush was charged with anhydrous $FeBr_2$ (12.9 g, 60 mmol), THF (500 ml), $P(OMe)_3$ (62 g, 500 mmol), and sodium amalgam (Na, 2.8 g, 120 mmol in 60 ml of Hg). The yellow-orange mixture turned brown as the reduction took place. The brown suspension was filtered through Celite and the filtrate was stripped to dryness on a vacuum line at room temperature. The dark solids were extracted with several 50-ml portions of pentane, chromatographed, and the resultant yellow solution was stripped to dryness, yielding $Fe[P(OMe)_3]_5$ in analytical purity (yields as high as 40%). The extreme solubility of the product makes recrystallization impractical. The material can be sublimed onto a liquid nitrogen cold finger under high vacuum with loss in yield: mp 158–160 °C dec.

Anal. Calcd for $FeP_5O_{15}C_{15}H_{45}$: Fe, 8.3; P, 22.9; O, 35.5; C, 26.7; H, 6.7. Found: Fe, 9.0; P, 24.3; O, 33.1; C, 27.0; H, 6.8.

(B) Pentakis(triethyl phosphite)iron(0). This compound is prepared and isolated in a manner analogous to that described in IA. The material can be recrystallized from acetone: mp 150–152 °C.

Anal. Calcd for $FeP_5O_{15}C_{30}H_{75}$: P, 17.5; O, 27.1; C, 40.7; H, 8.53. Found: P, 18.8; O, 29.0; C, 40.1; H, 8.28.

II. Ruthenium. (A) Pentakis(trimethyl phosphite)ruthenium(0). A flask was charged with $Ru[P(OCH_3)_3]_4Cl_2$[11] (2.0 g, 3.0 mmol), THF (40 ml), $P(OCH_3)_3$ (4 g, 32 mmol), and sodium amalgam (Na, 0.14 g; 6 mmol in 25 ml of Hg). The clear yellow solution became turbid as stirring was continued. The suspension was stripped under vacuum and the solids were extracted with pentane. The solution was chromatographed on alumina before reduction of volume and cooling to yield a white crystalline solid: mp 190 °C.

Anal. Calcd for $RuP_5O_{15}C_{15}H_{45}$: C, 25.0; H, 6.29; P, 21.5; O, 33.3. Found: C, 25.2; H, 6.13; P, 21.0; O, 32.1.

III. Osmium. (A) $OsCl_4[P(OCH_3)_3]_2$. Amalgamated zinc (excess) and Na_2OsCl_6 (4.5 g, 10 mmol) are added with stirring to a solution of 40 ml of tetrahydrofuran and $P(OCH_3)_3$ (10.0 g, 80 mmol). After stirring for 1 day, the entire solution was filtered through alumina and washed with tetrahydrofuran. The resulting solution was stripped to dryness to give a 25% yield (1.5 g, 2.5 mmol) of yellow powder of the stoichiometry $OsCl_4[P(OCH_3)_3]_2$. The material does not melt up to 300 °C.

Anal. Calcd for $OsP_2O_6C_6H_{18}Cl_4$: P, 10.7; C, 12.4; H, 3.13; Cl, 24.4. Found: P, 10.4; C, 12.73; H, 3.28; Cl, 23.46.

(B) Pentakis(trimethyl phosphite)osmium(0). In a nitrogen flush box, a 25-ml flask was equipped with a magnetic stirrer and charged with $OsCl_4[P(OCH_3)_3]_2$ (290 mg, 0.5 mmol), $P(OCH_3)_3$ (350 μl, 3.0 mmol), 10 ml of tetrahydrofuran, and 16 ml of sodium amalgam (0.125 M in sodium). After 4 h of stirring, the tetrahydrofuran solution was decanted off, stripped to dryness, and the resulting white solids were extracted with pentane. Stripping to dryness yielded white tacky solids which were used for the NMR studies without further purification.

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Interaction of Aquated *cis*-$[(NH_3)_2Pt^{II}]$ with Nucleic Acid Constituents. 1. Ribonucleosides

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Abstract: The extent of interaction of *cis*-$(NH_3)_2Pt^{II}$ with the ribonucleosides guanosine, adenosine, and cytidine at pH 6.5 has been studied. The apparent formation constants for the 1:1 complexes were determined at 25 °C utilizing ultraviolet difference spectroscopy. The log K values obtained are 3.7, 3.6, and 3.5, respectively. In all cases, the data are consistent with the nucleoside functioning as a monodentate ligand with no net deprotonation involved in the binding process. Metal binding at multiple sites on the nucleoside may occur at high *cis*-$(NH_3)_2Pt^{II}$/nucleoside mole ratios and also, for the extended incubation periods required in these studies, elevated temperatures appear to promote secondary reactions. Sites of binding are suggested and the implications of these results to the binding process at the polynucleotide level are discussed.

The study of the interaction of heavy metal complexes with biological moieties has recently seen an upsurge of interest due to studies concerned with methylation of heavy metals in aqueous environments,[1,2] investigations exploring the potential use of heavy metals to sequence nucleic acids using electron microscopy,[3] and recent attempts to understand the chemotherapeutic action of inorganic coordination complexes.[4,5]

The impetus for much of the present interest in the chemistry of *cis*-$(NH_3)_2PtCl_2$ came from the initial discovery by Rosenberg et al. that this complex not only inhibited replication in *E. coli* cells,[6,7] but also exhibited a broad spectrum of antitumor activity.[5,8-12] Although it has been generally realized that heavy metals do bind to nucleic acids, proteins, and the respective monomeric constituents, a number of studies have