$x^2 - y^2$ and the z^2 orbitals in the photoreactive state. Unfortunately, determination of the numerical value of θ is not straightforward, as it depends on the relative values of the σ parameters for all six ligands and the repulsion parameters, B and C, and requires a complete numerical state calculation.[51] Fortunately, θ is constrained to lie between $\pi/2$ and $3\pi/4$, and for *cis*-$[Cr(en)_2F(H_2O)]^{2+}$, there is little ambiguity in the interpretation of the calculation.

The equations used to determine the relative strengths of the Cr-ligand bonds (the bond indices) in the photoreactive states are[51]

$$I^*(ML_z) = 2\sigma_z + (2 - \cos^2\theta)\pi_z$$

$$I^*(ML_y) = 3\sigma_y + [2 - \cos^2(\theta - \pi/3)]\pi_y$$

$$I^*(ML_x) = 3\sigma_x + [2 - \cos^2(\theta + \pi/3)]\pi_x$$

The values of the bond indices clearly depend on the value of θ, but it turns out that the exact value of θ has little effect on the predicted photochemistry of *cis*-$[Cr(en)_2F(H_2O)]^{2+}$. As shown in Figure 6, the weakest Cr-ligand bonds are the $Cr-OH_2$ and the Cr-N bonds (on the x axis) throughout the posssible range for θ. The indices for these two ligands are so similar that it may be overextending the model to choose between them; at their maximum separation, when $\theta = 2\pi/3$, $I^*(M-OH_2) = 7440$ cm^{-1} and $I^*(M-N_x) = 7180$ cm^{-1}. For very small values of θ (between 90 and 92.7°), the index for the $Cr-OH_2$ bond is slightly less than that of the Cr-N bond, while, throughout most of the permissible region for θ (92.7-135°), the Cr-N bond has the lower bond index.

These calculations imply that either photoinduced Cr-N or $Cr-OH_2$ bond cleavage would be expected. While this analysis clearly rules out photoinduced Cr-F bond cleavage, the lack of detailed stereochemical information about the photoreaction prevents a critical evaluation of the theoretical model. Photoinduced water release could only be detected if isomerization to *trans*-$[Cr(en)_2F(H_2O)]^{2+}$ occurred; the spectrum of this ion is known to have a peak at about 457 nm,[31] and we could find no evidence of such a band. Stereoretentive water exchange would, of course, not have been detectable. Thus, the observed amine release is consistent with the Vanquickenborne model, but information on the stereochemistry of the photoinduced amine release would provide a more demanding test of the model.

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Registry No. *cis*-$[Cr(en)_2F_2]^+$, 22432-37-7; *cis*-$[Cr(en)_2F(H_2O)]^{2+}$, 34431-44-2.

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Temperature-Jump Relaxation Study of the Zn^{2+}-Chlorophenol Red System

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A temperature-jump relaxation study was carried out on the system Zn^{2+}-chlorophenol red in an attempt to locate the octahedral/tetrahedral conversion involving the aquo ion. A single relaxation time (50-100 μs) was observed. The detailed concentration and pH dependences were consistent with a series of coupled protolysis/hydrolysis/proton-exchange steps. The observed relaxation time corresponded essentially to the reactions $ZnOH^+ + H^+ \rightleftharpoons Zn^{2+}$ and $ZnOH^+ + HIn \rightleftharpoons Zn^{2+} + In^-$, for which the forward rate constants were 2.2×10^{10} and 1.0×10^8 M^{-1} s^{-1}, respectively. These are comparable to analogous rate constants in other proton-transfer reactions. We conclude that any structural change involving Zn^{2+} does not occur to an extent that permits kinetic detection.

Introduction

In recent years our laboratory has carried out a series of rapid kinetic studies involving divalent metal and ligands such as amino acids[1] and nucleotides.[2,3] Work to date has primarily focused on the metal ions Ni^{2+}, Cu^{2+}, and Mg^{2+}.

Some years ago we carried out a temperature-jump relaxation study involving the complexation kinetics of Zn^{2+} with glycine.[4] The rate constant for the formation of the $Zn(gly)^+$ complex (two coordination sites bound) was "normal". That is, its value was consistent with the rate of displacement of solvent molecules from the primary coordination sphere of the metal ion. An unusual feature of that study was that the formation of the second (bis) complex seemed to be associated with a slow interconversion; we tentatively attributed this to a structural change involving the metal ion. Although there have been other kinetic studies involving Zn^{2+} by *T*-jump[5,6] and ultrasonic methods,[7,8] no "normal" *bis* complexation rate has been observed for ligands of coordinating ability of 2 or more. Recent Raman IR data[9] and statistical interpretation[10] of Zn^{2+}-binding constants support the concept of an octahedral-tetrahedral structural change for the Zn^{2+} aquo ion. Nevertheless, despite several attempts to detect (and one report[11] of) the kinetics of the structural change in aqueous Zn^{2+}, it has to date eluded actual observation.

More recently, we have turned our attention to the complexation kinetics of Zn^{2+} with other ligands[12] via temperature-jump spectroscopy. When "blanks" were tested (solutions lacking one component of the metal ion-indicator-ligand system), the blank consisting of Zn^{2+} and indicator often showed a relaxation effect in the 10^{-4}-s time region over the pH range 6-7. Under optimal conditions this effect had a very large amplitude (Figure 1). We felt it was necessary to know the cause of this effect prior to continuing the complexation studies with Zn^{2+}. In addition, there was the possibility that this could be the long-sought structural change postulated in aqueous Zn^{2+}. For these reasons, we carried out this detailed study of the Zn^{2+}-chlorophenol red system.

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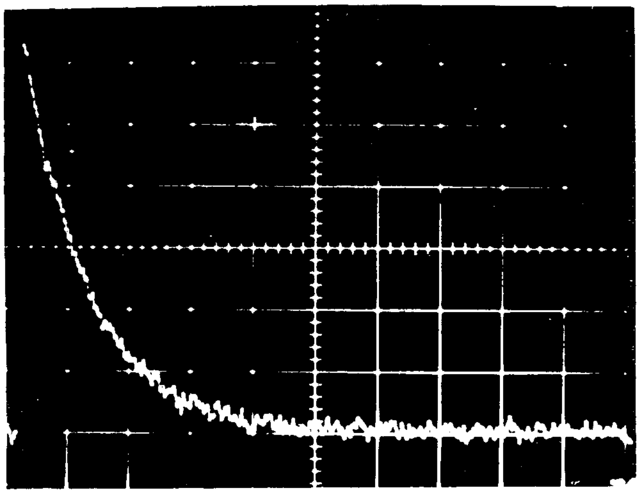


Figure 1. Relaxation trace in the Zn^{2+}–CPR system. Conditions: $[Zn^{2+}] = 0.01$ M; $[CPR] = 4 \times 10^{-5}$ M; pH 6.30; monitoring wavelength 575 nm at 10 °C. Horizontal axis: 50 μs/cm.

Materials and Methods

A 1.0 M Zn^{2+} stock solution was prepared from reagent grade $Zn(NO_3)_2 \cdot 6H_2O$ and passed through a 0.45-μm Millipore filter. The concentration was checked by atomic absorption spectroscopy. A 1.0 mM stock solution of the purified indicator chlorophenol red (CPR) was prepared and filtered in the same manner. Experimental solutions were prepared daily from these stock solutions. Typically, samples contained $Zn(NO_3)_2$ in the concentration range 2.5–100 mM, whereas the concentration of the indicator CPR was maintained at 40 μM. The pH of the solutions was adjusted by addition of HNO_3 and KOH with a micropipet.

The relaxation data were obtained with a temperature-jump spectrometer (Messanlagan Studiengesellschaft)[13] at 10 °C and $I = 0.1$ N KNO_3. The experimental technique consisted of equilibrating sample solutions at 5 °C in the temperature-jump cell; the temperature reequilibration time was about 20 min. A 35-kV discharge was then passed through the experimental solution, yielding a 5 °C temperature rise within a few microseconds. The resultant relaxation traces, monitored via transmittance changes at the absorption maximum of CPR (572 nm), were stored on a Biomation 802 transient recorder, displayed on an oscilloscope screen, and photographed. The digitized data were then transmitted to a microcomputer for storage on a floppy disk and subsequently analyzed by our program EFIT for the relaxation time.[14] At least three relaxation curves were obtained for each pH/concentration point; precision was typically ±10%, and often better. The pH was the primary source of uncertainty, since working with an unbuffered system in the range of pH 6–7 resulted in a small pH drift. The pH of the solution was recorded after each temperature-jump experiment.

Results and Discussion

A single relaxation effect was observed in the 50-μs time region (Figure 1). The complete set of initial concentrations and relaxation times is given in Table II. The effect disappeared with the removal of either the metal ion or the indicator. Separate experiments established that the relaxation time was independent of the nitrate ion concentration. Experiments were reproducible after repeated microfiltration, thus establishing that the effect was not an artifact from possible precipitation. The relaxation time demonstrated a weak dependence on zinc ion concentration: τ^{-1} increased only by about a factor of 2 with a 20-fold increase of the initial metal ion concentration (see Table II and Figure 2). This concentration dependence was not readily apparent until rather high concentrations of metal ion were used. The amplitude of this relaxation effect was very sensitive to the initial zinc concentration: reliable relaxation values could not be obtained for solutions with total zinc concentrations less than 2.5×10^{-3} M. Changing the indicator concentration by as little as a factor of 2 in either direction resulted in amplitudes unsuitable for analysis.

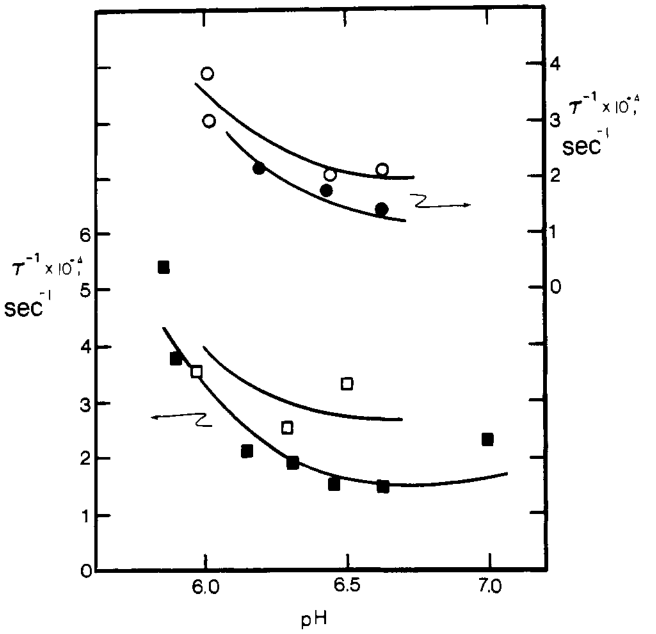
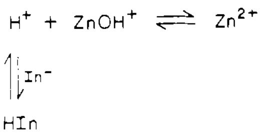


Figure 2. Concentration and pH dependence of the relaxation time for Zn^{2+}–CPR: ■, $[Zn^{2+}] = 0.01$ M; □, $[Zn^{2+}] = 0.04$ M; ●, $[Zn^{2+}] = 0.005$ M; ○, $[Zn^{2+}] = 0.02$ M.

Scheme I



$$\begin{tikzcd} H^+ \arrow[d, shift left, "In^-"] \arrow[d, leftarrow, shift right] & + \ ZnOH^+ \arrow[r, shift left] & Zn^{2+} \arrow[l, shift left] \\ HIn & & \end{tikzcd}$$

The data at various metal ion concentrations are shown as a function of pH in Figure 2. A nearly parabolic pH dependence was observed within the interval of study, pH 5.8–6.9, the minimum or plateau region being located at about pH 6.6–6.8. The relaxation effect became dramatically faster below pH 5.9, approaching the time resolution of the instrument around pH 5.7.

Several relatively simple mechanisms were tested and shown to be inconsistent with the relaxation data. Our efforts to fit the data to a one-step isomerization process involving the tetrahedral and octahedral forms of aqueous zinc were unsuccessful. Such a scheme predicted a relaxation time independent of both metal concentration and pH. Despite our observed effect's slight dependence on the zinc concentration, the parabolic pH dependence was incompatible with a proposed isomerization reaction. Second, a mechanism of proton transfer involving Zn^{2+} coupled to a rapid indicator ionization (Scheme I), predicted a strong and nearly linear τ^{-1} independence on the overall zinc concentration. Third, a reaction scheme involving metal ion binding to the indicator was eliminated because (a) UV/visible difference spectroscopy and pH titration experiments showed no evidence of binding and (b) the dependence on Zn^{2+} predicted for such a mechanism was inconsistent with the results.

The observed relaxation behavior shown in Figure 2 is strikingly similar to that of a system previously characterized[15] in our laboratory. This is the inosine–CPR system, which showed a single relaxation effect in the same time region as that of the present study. The obvious structural differences between the nucleoside *inosine* and the metal ion *zinc* mask their similarity with respect to proton ionization. Inosine has a pK_a of 8.9, which is comparable to the Zn^{2+} value of approximately 9[16] under similar conditions. The mechanism proposed for the earlier study involved a proton transfer between the nucleoside and indicator and protolysis/hydrolysis of the indicator. We found that the same mechanism

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Scheme II

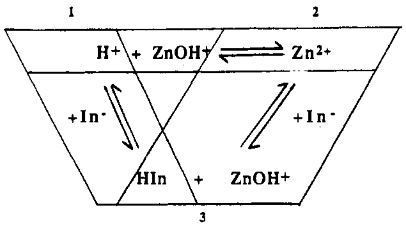

Table I. Equilibrium Constants for the Zn^{2+}–CPR System[a]

step	reaction	log K
2–1	$Zn^{2+} \rightleftharpoons ZnOH^+ + H^+$	–9.0[b]
3–1	$HIn \rightleftharpoons H^+ + In^-$	–6.1
3–2	$HIn + ZnOH^+ \rightleftharpoons In^- + Zn^{2+}$	3.0[c]

[a] At or near 10 °C and I = 0.1 M. [b] Reference 16. [c] Related to the other equilibrium constants by the relationship $K_{32} = K_{31}/K_{21}$.

could quantitatively account for the Zn^{2+}–CPR kinetic data (see Scheme II). This triangular mechanism involves three coupled steps: 1–2, proton transfer of $ZnOH^+$ with H^+ to yield free hydrated Zn^{2+}; 1–3, the corresponding indicator protonation/deprotonation; 2–3 proton exchange between Zn^{2+} and HIn. There are two independent reactions, and hence two relaxation times, for Scheme II. Two first-order (close-to-equilibrium) rate equations can be written upon the choice of two independent concentration variables. If one picks $\delta[Zn^{2+}]$ and $\delta[In^-]$, the rate equation can be cast in the form

$$\frac{d\delta[Zn^{2+}]}{dt} = a_{11}\delta[Zn^{2+}] + a_{12}\delta[In^-] = -\frac{1}{\tau}\delta[Zn^{2+}] \quad (1)$$

$$\frac{d\delta[In^-]}{dt} = a_{21}\delta[Zn^{2+}] + a_{22}\delta[In^-] = -\frac{1}{\tau}\delta[In^-] \quad (2)$$

where a_{ij} coefficients are given by

$$\begin{aligned} a_{11} &= -(k_{12}([ZnOH^+] + [H^+]) + k_{21} + k_{23}[In^-] + k_{32}[HIn]) \\ a_{12} &= k_{12}[ZnOH^+] - k_{23}[Zn^{2+}] - k_{32}[ZnOH^+] \\ a_{21} &= k_{13}[In^-] - k_{32}[HIn] - k_{23}[In^-] \quad (3) \\ a_{22} &= \\ &-(k_{13}([H]^+ + [In^-]) + k_{31} + k_{32}[ZnOH^+] + k_{23}[Zn^{2+}]) \end{aligned}$$

Equations 1–3 yield a 2 × 2 determinant, the solution to which is

$$\frac{1}{\tau_\pm} = \frac{-(a_{11} + a_{22}) \pm [(a_{11} + a_{22})^2 - 4(a_{11}a_{22} - a_{21}a_{12})]^{1/2}}{2} \quad (4)$$

where τ_+ and τ_- are the two relaxation times resulting from the + and – signs in eq 4. There are a total of six rate constants in the determinant coefficients a_{ij}. Elimination of the reverse rate constants by the use of the appropriate equilibrium constants (Table I) reduces the variables to three. Of these, the rate constant for the indicator protonation (k_{13}) is known from an earlier study[15] in our laboratory under the same experimental conditions. This constant was fixed in eq 4, and a computer was programmed to minimize the error function χ^2 via the nonlinear-least-squares program KRUNCH.

The two relaxation times predicted by eq 4 are on the order of 10^{-4}–10^{-5} s. Although they are closely kinetically coupled, τ_1 was found to be more sensitive to the (known) indicator rate constant k_{13}, and τ_2 to the two unknown rate constants k_{12} and k_{23}. The slower rate (τ_2^{-1}) corresponded to the observed relaxation times for the Zn^{2+}–CPR system. Table II shows the good fit obtained between the experimental relaxation times and those predicted by eq 4. Several runs were carried out as a function of pH at fixed Zn^{2+} concentrations; these data are displayed in Figure 2, with the solid lines calculated from eq 4. The best-fit rate constants obtained by the least-squares fitting procedure are listed in Table III.

Table II. Concentration and pH Dependence of the Relaxation Time[a,b]

$[Zn^{2+}]_0$, M	pH[c]	$10^{-3}\tau^{-1}$, s^{-1} (obsd)	$10^{-3}\tau^{-1}$, s^{-1} (calcd)[d]
0.100	6.29	37.3	40.3
0.100	6.40	41.3	39.7
0.060	6.40	29.0	32.3
0.060	6.54	33.6	32.1
0.040	5.97	35.1	41.8
0.040	6.29	25.0	29.4
0.040	6.50	32.0	27.0
0.020	6.01	38.8	35.2
0.020	6.06	30.1	32.5
0.020	6.44	20.5	21.6
0.020	6.62	21.4	20.0
0.010	5.85	54.0	44.2
0.010	5.90	37.8	40.1
0.010	6.15	21.0	25.4
0.010	6.29	18.9	20.4
0.010	6.45	15.2	16.8
0.010	6.63	14.6	14.9
0.010	6.95	23.0	15.5
0.005	6.19	21.6	21.9
0.005	6.43	17.6	14.7
0.005	6.62	14.1	11.7
0.0025	6.49	14.8	12.0

[a] At 10 °C and I = 0.1 M. [b] Indicator concentration was 40 μM in all cases. [c] C_H was calculated with γ_H = 0.83. [d] Slower rate from eq 4.

Table III. Best-Fit Rate Constants for the Zn^{2+}–CPR System[a]

step[b] 1–2: $ZnOH^+ + H^+ \rightleftharpoons Zn^{2+}$	
	$k_{12} = 2.2 \times 10^{10}\ M^{-1}\ s^{-1}$
	$k_{21} = 2.2 \times 10\ s^{-1}$
step 2–3: $ZnOH^+ + HIn \rightleftharpoons Zn^{2+} + In^-$	
	$k_{32} = 1.0 \times 10^{8}\ M^{-1}\ s^{-1}$
	$k_{23} = 1.0 \times 10^{5}\ M^{-1}\ s^{-1}$
step 1–3: $H^+ + In^- \rightleftharpoons HIn$	
	$k_{13} = 2.1 \times 10^{10}\ M^{-1}\ s^{-1}$

[a] At 10 °C and I = 0.1 M. [b] Numbering system refers to Scheme II.

The constants for steps 3–2 and 1–2 can be briefly discussed in terms of analogous constants for similar systems.

The two rate constants for the exchange reaction

$$ZnOH^+ + HIn \underset{k_{23}}{\overset{k_{32}}{\rightleftharpoons}} Zn^{2+} + In^-$$

are 1.0 × 10^8 and 1.2 × 10^5 $M^{-1}\ s^{-1}$, respectively. These are similar to rate constants for CPR and the deprotonated and protonated forms of inosine (k_{32} and k_{23} = 5.9 × 10^8 and 4.3 × 10^5 M s^{-1}, respectively) that we reported some years ago.[15] The pK values of Zn^{2+}(aq) and protonated inosine are almost identical (9.0 and 8.96). Rate constants for proton exchange among a series of similar ions and molecules are principally dependent on the pK difference between the proton donor and acceptor. Consequently, it is not surprising that Zn^{2+} behaves similarly to inosine.

A few comments can now be made about the protonation reaction involving $ZnOH^+$. The best-fit rate constant for the reaction $ZnOH^+ + H^+ \rightarrow Zn^{2+}$(aq) is 2.2 × 10^{10} $M^{-1}\ s^{-1}$. We were somewhat surprised to find that only a few other hydroxymetal ion reactions have been measured to date. Among them are the univalent hydroxy reactions

$$CuOH^+ + H^+ \qquad k_{12} = \sim 1 \times 10^{10}\ M^{-1}\ s^{-1} \quad \text{[ref 17]}$$

$$UO_2OH^+ + H^+ \qquad k_{12} = 1.65 \times 10^{10}\ M^{-1}\ s^{-1} \quad \text{[ref 18]}$$

The value reported for the $CuOH^+$ system is an approximate value determined by an early ultrasonic study. Given the different conditions of the experiments, we feel that the three systems have the same value of k_{12} within experimental error: (1–2) × 10^{10}

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M^{-1} s^{-1}. The corresponding values for doubly charged hydroxy cations are, as expected, somewhat slower: 4.4 × 10^9 and 7.8 × 10^8 M^{-1} s^{-1} for $AlOH^{2+}$ [19] and $CrOH^{2+}$,[20] respectively. The values predicted by the Smoluchowski–Eigen equation[17] for the diffusion-controlled reaction of like charges are strongly dependent on the "distance parameter" in the equation. For the reasonable encounter distances of 4–6 Å, the equation would predict k_E = (1.2–2.4) × 10^{10} and (5–10) × 10^9 M^{-1} s^{-1} for the +1,+1 and +2,+1 charge interactions, respectively. These are close to the measured values; it is likely, therefore, that all these proton transfers are encounter-controlled reactions.[21]

Finally, we return to the question originally addressed in this study: Where is the structural transition proposed in aqueous Zn^{2+}? Such a transition, for which there is considerable evidence, presumably is an octahedral/tetrahedral conversion. As demonstrated above, the detailed concentration and pH dependences of the effect we have characterized are quantitatively explained in terms of more conventional proton transfers (Scheme II). Nearly 20 years ago,[11] a relaxation effect at about 10^{-1} s was attributed to a structural transition in Zn^{2+}. Our own work, with instrumentation of greatly increased sensitivity, does not confirm that earlier study. The only kinetic evidence, in fact, for the existence of a structural transition in Zn^{2+} is the *lack* of the observation of a "normal" bis-complexation rate for Zn(II) complexes with ligands of denticity equal to 2 or more.[4] Irish and Jarv[9] carried out Raman IR measurements in 5 *m* Zn^{2+} and observed spectral bands and shifts that were consistent with the octahedral/tetrahedral interconversion $Zn(H_2O)_6^{2+} \rightleftharpoons Zn(H_2O)_4^{2+} + 2H_2O$. They proposed that the tetrahedral form was favored at the higher temperatures (>200 °C) of the study in 5 *m* aqueous solution. King[10] carried out a detailed analysis of zinc equilibria and was able to estimate the ratio of tetrahedral/octahedral Zn^{2+} ions to be about 0.0029 (presumably near 25 °C). He also showed that the fraction of Zn^{2+} tetrahedrally coordinated would increase as the number of bound ligands (other than water) increased. These structural conclusions are all consistent with our inability to observe the structural change in aqueous Zn^{2+} solutions. It is entirely possible that the transition is not favored in $Zn(H_2O)_6^{2+}$ per se but occurs only after two or more coordination sites on the metal ion are substituted by ligands other than water. In any event, the structural change in aqueous Zn(II) continues to elude direct observation by kinetic means.

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Registry No. CPR, 4430-20-0; Zn^{2+}, 23713-49-7; $ZnOH^+$, 22569-48-8; H^+, 12408-02-5.

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A New Class of Inorganic Heterocycles from Insertion of Transition Metals into the Cyclophosphazene Skeleton. Synthesis and Characterization of Six-Membered Rings with Vanadium, Tungsten, and Rhenium in High Oxidation States

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The linear phosphazene salt $[H_2NPPh_2NPPh_2NH_2]^+Cl^-$ (**1**) reacts with VCl_4, WBr_4, WF_6, and $ReCl_5$ to form the cyclometallaphosphazenes $\overline{NPPh_2NPPh_2NV}Cl_2$ (**4**), $\overline{NPPh_2NPPh_2NW}Br_3$ (**5**), $\overline{NPPh_2NPPh_2NW}F_3$ (**6**), and $\overline{NPPh_2NPPh_2NRe}Cl_4$ (**7**), respectively. The cyclotungstaphosphazene $\overline{NPPh_2NPPh_2NW}Cl_3$ (**3**) undergoes a metathetical halogen-exchange reaction with NaF or AgF to give **6** in high yield and purity. The stability of the transition metals in their high oxidation state in the phosphazene skeleton has been demonstrated. ^{19}F, ^{31}P, and ^{51}V NMR spectroscopic investigations confirm the structures of the cyclometallaphosphazenes.

Introduction

The chemistry of phosphazenes has been the subject of extensive research in recent years. The majority of investigations concerning this area have been on the reactions of halogenophosphazenes, both cyclic and polymeric, with a wide range of nucleophiles that includes aryloxides, alkoxides, amines, and organolithium or Grignard reagents.[1,2] The synthesis of phosphazene derivatives containing transition metals bonded exocyclically to the phosphazene ring may be noted as one of the most significant contributions in this field in the last few years.[3-6]

The synthesis of cyclometallaphosphazenes, cyclophosphazenes containing transition metals as part of the ring skeleton, is an area yet unexplored. In recent communications we have reported the syntheses and structures of cyclomolybda- (**2**) and cyclotungstaphosphazenes (**3**) employing two different synthetic approaches.[7,8] One involves the reaction of the transition-metal halide with the linear phosphazene salt $[H_2NPPh_2NPPh_2NH_2]^+Cl^-$ (**1**). Another route involves the 1,4-cycloaddition of the transition-metal nitrido chloride with **1**.

The new heterocyclic compounds **2** and **3** are the first examples possessing a direct covalent σ-bond linkage between a transition metal and skeletal nitrogen atoms of a phosphazene ring. These compounds give rise to an extensive chemistry with structural

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