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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[19] Holmes, L. P.; Cole, D. L.; Eyring, E. M. *J. Phys. Chem.* **1968**, *72*, 301.
[20] Rich, L. D.; Cole, D. L.; Eyring, E. M. *J. Phys. Chem.* **1969**, *73*, 713.
[21] There appears to be no entirely convincing explanation for the 6-fold difference in k_{12} for $CrOH^{2+}$ vs. $AlOH^{2+}$.

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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

Kattesh V. Katti, Herbert W. Roesky,* and Mathias Rietzel

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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 $NPPh_2NPPh_2NVCl_2$ (**4**), $NPPh_2NPPh_2NWBr_3$ (**5**), $NPPh_2NPPh_2NWF_3$ (**6**), and $NPPh_2NPPh_2NReCl_4$ (**7**), respectively. The cyclotungstaphosphazene $NPPh_2NPPh_2NWCl_3$ (**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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[1] Allcock, H. R. *Phosphorus–Nitrogen Compounds*; Academic: New York, 1972.
[2] Krishnamurthy, S. S.; Sau, A. C.; Woods, M. In *Advances in Inorganic Chemistry and Radiochemistry*; Emeleus, H. J., Sharpe, A. G., Eds.; Academic: New York, 1978; Vol. 21, pp 41–112.
[3] Greigger, P. P.; Allcock, H. R. *J. Am. Chem. Soc.* **1979**, *101*, 2492.
[4] Allcock, H. R.; Greigger, P. P.; Wagner, L. J.; Bernheim, M. Y. *Inorg. Chem.* **1981**, *20*, 716.
[5] Allcock, H. R.; Wagner, L. J.; Levin, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 1321.
[6] Allcock, H. R.; Riding, G. H.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 5561.
[7] Roesky, H. W.; Katti, K. V.; Seseke, U.; Schmidt, H. G.; Egert, E.; Herbst, R.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1987**, 847.
[8] Roesky, H. W.; Katti, K. V.; Seseke, U.; Witt, M.; Egert, E.; Herbst, R.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 477.

0020-1669/87/1326-4032$01.50/0

diversity since (i) they are expected to provide valuable information about the bonding within the phosphazene ring, (ii) they are potential precursors for the synthesis of transition-metal-incorporated phosphazene polymers, and (iii) these stable cyclic derivatives offer scope for generating varieties of organometallic compounds.

We report in this paper syntheses of new cyclometallaphosphazenes containing vanadium and rhenium. We also describe how cyclotungstaphosphazene containing tungsten–fluorine or tungsten–bromine bonds can be obtained by using the corresponding halides of the metal.

Experimental Section

Materials. All experimental manipulations were performed under an atmosphere of dry nitrogen. Solvents were dried and distilled prior to use. The linear phosphazene salt $[H_2NPPh_2NPPh_2NH_2]^+Cl^-$ (**1**)[9] and VCl_4[10] were prepared as described in the literature. WBr_4, WF_6, and $ReCl_5$ were obtained from Fluka chemicals.

Equipment. WF_6 and **1** were reacted in a Monel cylinder. ^{19}F, ^{31}P, and ^{51}V NMR spectra were obtained by means of a Bruker AM 250 instrument using $CFCl_3$, 85% H_3PO_4, and $VOCl_3$ as external standards, respectively. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer. Mass spectrometric analyses were performed with a Finnigan MAT 8230 instrument. The elemental microanalyses were carried out by Beller, Göttingen, FRG.

Preparation of $NPPh_2NPPh_2NVCl_2$ (4). Anhydrous **1** (5.65 g; 12.5 mmol) was added to a solution of VCl_4 (2.70 g; 14 mmol) in 200 mL of CCl_4. The mixture was heated under reflux with continuous Cl_2 bubbling for 24 h. The solvent was removed in vacuo, and the resultant red solid was recrystallized three times from dry acetonitrile to obtain pure **4** (yield 3.60 g, 54%; red crystals; mp 175 °C dec).

Anal. Calcd for $C_{24}H_{20}Cl_2N_3P_2V$: C, 54.03; H, 3.77; N, 7.87; Cl, 13.30. Found: C, 53.7; H, 3.7; N, 7.8; Cl, 13.4. MS (EI, *m/z*): 533 (M^+, 100%). $^{31}P\{^1H\}$ NMR (CH_3CN, CD_3CN; external 85% H_3PO_4): δ 43.7 (s). ^{51}V NMR (CH_3CN; external $VOCl_3$): δ 46.8 (s).

Preparation of $NPPh_2NPPh_2NWBr_3$ (5). Anhydrous **1** (1.85 g; 4.1 mmol) was added to a suspension of WBr_4 (2.07 g; 4.1 mmol) in 150 mL of liquid bromine. The mixture was heated under reflux for 24 h. Bromine was removed by distillation, and the brown residue was dried in vacuo. This residue was recrystallized twice from dry acetonitrile to obtain **5** in the form of dark brown crystals (yield 2.19 g; 64%; mp 210 °C dec).

Anal. Calcd for $C_{24}H_{20}Br_3N_3P_2W$: C, 34.45; H, 2.41; N, 5.03; Br, 28.67. Found: C, 34.4; H, 2.3; N, 4.9; Br, 29.5. MS (EI, *m/z*): 836 (M^+, 100%). $^{31}P\{^1H\}$ NMR (CH_3CN, CD_3CN; external 85% H_3PO_4): δ 43.8 (s).

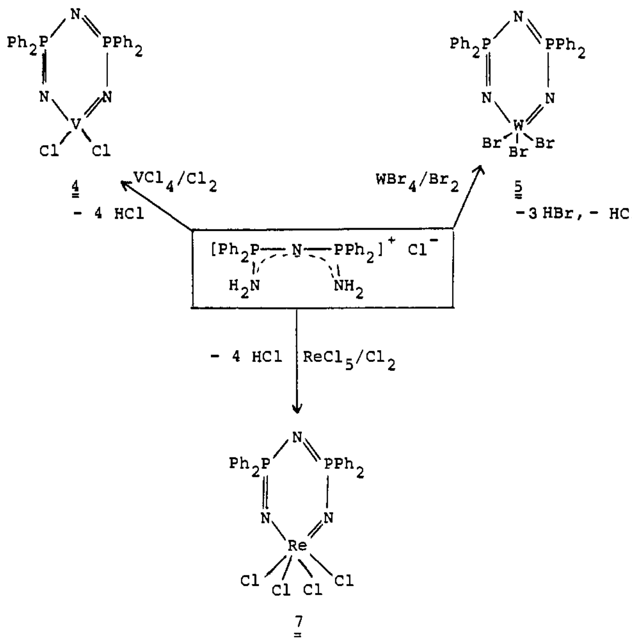
Note: The synthesis of **5** was carried out by wearing gloves in a fume hood. The small quantities of spilled bromine and the residual bromine left after drying **5** in vacuo were absorbed by using a 1:1:1 mixture by weight of calcium carbonate, clay cat litter (bentonite), and sand. This mixture was slowly added to a pail of cold water to which 10% sodium bisulfite was added until the solution turned colorless. This solution was brought to neutral pH by adding a small amount of calcium carbonate and drained off by flushing with large quantities of water.

Preparation of $NPPh_2NPPh_2NWF_3$ (6). A freshly recrystallized sample of **3** (1.27 g; 1.8 mmol) was suspended in 250 mL of dry acetonitrile. To this suspension was added a dry sample of sodium fluoride (2.27 g; 54 mmol). The mixture was heated under reflux for 24 h and filtered after cooling. The filtrate was evaporated and dried in vacuo to obtain a grey solid (0.55 g). The powdery residue, which contained the unreacted sodium fluoride, was subjected to Soxhlet extraction using dry acetonitrile (250 mL) for 10 h. Evaporation of the acetonitrile extract yielded a grey solid (0.75 g). These two crops from the filtrate and the residue showed similar ^{19}F and $^{31}P\{^1H\}$ NMR spectra. Recrystallization from dry acetonitrile gave the pale yellow crystalline product **6** (total yield 0.88 g, 75%; mp 195 °C dec).

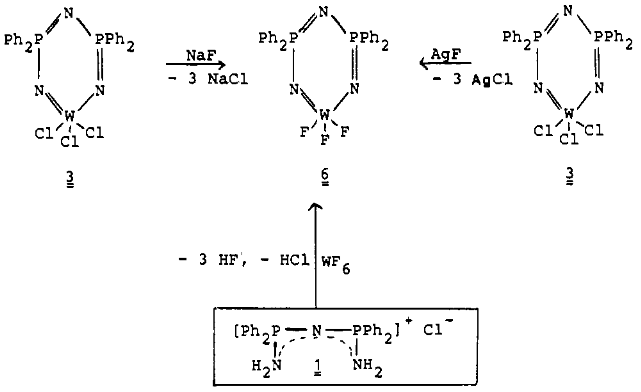
Anal. Calcd for $C_{24}H_{20}F_3N_3P_2W$: C, 44.10; H, 3.09; N, 6.43; F, 8.73. Found: C, 43.9; H, 3.1; N, 6.3; F, 8.6. MS (EI, *m/z*): 653 (M^+, 100%). $^{31}P\{^1H\}$ NMR (CH_3CN, CD_3CN; external 85% H_3PO_4): δ 22.5 (s). ^{19}F NMR (CH_3CN; external $CFCl_3$): $\delta(F_a)$ 48.8 (d); $\delta(F_e)$ −82.6 (t) [$^2J(^{19}F_a-^{19}F_e)$ = 53 Hz; $^1J(^{19}F-^{183}W)$ = 71 Hz].

The experimental procedure to obtain **6** by using silver fluoride as the fluorinating agent is the same as described above. Compound **6** was obtained in 70% yield.

Scheme I



Scheme II



Reaction of WF_6 with 1. A Monel cylinder containing **1** (4.21 g; 9.3 mmol) in 200 mL of dichloromethane was maintained at −78 °C. WF_6 (3.13 g; 10.5 mmol) was condensed into this cylinder. The mixture was allowed to warm to room temperature and then heated under reflux using a metal condenser. After 24 h the solvent was removed in vacuo to obtain a white solid. The ^{19}F NMR (CH_3CN, external $CFCl_3$) spectrum consisted of a complex multiplet, a doublet, and a triplet centered at δ 68.7, 48.8, and −82.6, respectively. The ^{31}P NMR (CH_3CN, CD_3CN; external 85% H_3PO_4) showed a single resonance line at δ 22.5 and signals characteristic of an AB spin system between δ 38 and 48. The relative intensities of the various signals in the ^{19}F and ^{31}P NMR spectra and comparison of these spectra with that of an authentic sample of **6** revealed that compound **6** was formed in 55% yield.

Preparation of $NPPh_2NPPh_2NReCl_4$ (7). Anhydrous **1** (3.30 g; 7.3 mmol) was added to a suspension of $ReCl_5$ (2.65 g; 7.3 mmol) in 250 mL of CCl_4. The mixture was heated under reflux with continuous Cl_2 bubbling for 24 h. The solvent was removed in vacuo, and the resultant brown solid was recrystallized three times from dry acetonitrile to obtain pure **7** (yield 3.35 g, 62%; pink crystals; mp 190 °C dec).

Anal. Calcd for $C_{24}H_{20}Cl_4N_3P_2Re$: C, 38.90; H, 2.72; N, 5.68; Cl, 19.20. Found: C, 38.7; H, 2.6; N, 5.7; Cl, 19.2. MS (EI, *m/z*): 739 (M^+, 100%). $^{31}P\{^1H\}$ NMR (CH_3CN, CD_3CN; external 85% H_3PO_4): δ 46.2 (s).

Results and Discussion

General Reactions. The linear phosphazene salt **1** reacts with VCl_4 (under Cl_2 atmosphere), WBr_4 (in liquid Br_2), WF_6, and $ReCl_5$ (under Cl_2 atmosphere) to give cyclometallaphosphazenes **4–7**, respectively (Schemes I and II). All these reactions proceed through the elimination of 4 mol of the hydrogen halide to afford the hydrogen-free metallacycles **4–7**. The multifunctionality of

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[9] Herring, D. L.; Douglas, C. M. *Inorg. Chem.* **1964**, *3*, 428.

[10] Funk, H.; Weiss, W. *Z. Anorg. Allg. Chem.* **1958**, *295*, 327.

the reactants involved in these reactions requires high dilutions by the solvents in order to obtain higher yields of products **4**–**7**; lower dilutions led to the formation of insoluble cross-linked polymeric products. In fact, the conditions described in the Experimental Section are the results of several experiments to obtain metallacycles **4**–**7** in maximum yields.

Synthesis and Characterization of $\overline{NPPh_2NPPh_2NVCl_2}$ (4). The linear phosphazene salt **1** reacts with VCl_4 in an atmosphere of dry chlorine in refluxing CCl_4 to give **4** in 55% yield (Scheme I). When this reaction was carried out in the absence of elemental chlorine, only the unsymmetrically substituted acyclic VCl_4 salt of **1** results as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy. From acetonitrile were obtained dark red crystals of **4**, which melt with decomposition at 175 °C. **4** is air-stable in the crystalline state, but solutions of **4** decompose slowly on exposure to air.

Characteristic absorptions for P–N bonds were found between 1140 and 1280 cm^{-1} in the infrared spectrum of **4**. The electron ionization mass spectrum of **4** showed the parent ion (m/z 533) with the expected isotopic mass pattern. The elemental analysis was compatible with structure **4**. The ^1H-decoupled ^{31}P NMR spectrum of **4** showed a sharp singlet at 43.7 ppm. The ^{51}V NMR spectrum consisted of a single resonance line at 46.8 ppm. This value of the ^{51}V NMR chemical shift is in accord with the range of chemical shifts expected for vanadium compounds in oxidation state V.[11]

We have been so far unsuccessful in determining the X-ray crystal structure of **4** because of the poor quality of crystals obtained for this compound.

Synthesis and Characterization of $\overline{NPPh_2NPPh_2NWBr_3}$ (5). Tungsten tetrabromide, when allowed to react with **1** in liquid bromine, resulted in the formation of **5** in 62% yield. From acetonitrile were obtained transparent dark brown crystals of **5**, which melt with decomposition at 210 °C. **5** is air-sensitive and turns immediately to a sticky blue mass when exposed to moisture.

The infrared spectral data of **5** are similar to those of the chloro analogue (**2**) except that the ν(W–Br) absorption band can be easily seen at a lower wavenumber compared to ν(W–Cl). The electron ionization mass spectrum of **5** consisted of the parent ion (m/z 836) with the expected isotopic mass pattern. The elemental analysis is in agreement with structure **5**. The $^{31}P\{^1H\}$ NMR spectrum showed a single line at 43.8 ppm.

Synthesis and Characterization of $\overline{NPPh_2NPPh_2NWF_3}$ (6). As shown in Scheme II, compound **6** can be obtained from three different methods. Tungsten hexafluoride reacts with **1** in an all-metal apparatus to give the cyclotungstaphosphazene **6** along with unidentified WF_6 substituted salts of **1**, as evidenced by ^{19}F and $^{31}P\{^1H\}$ NMR spectroscopy. However, the relative integrations (both ^{19}F and $^{31}P\{^1H\}$ NMR) revealed that **6** was present up to 55% in the reaction mixture. An elegant route to obtain **6** involves the direct metathetical exchange reactions of **3** using NaF or AgF. This method affords compound **6** in high purity and also in good yield.

6 is a pale yellow crystalline solid stable in the atmosphere at 25 °C. It can be readily stored in glass bottles, and it melts at 220 °C, giving a black residue.

The infrared spectral data of **6** are similar to those of its chloro (**3**) or bromo (**5**) derivatives except that ν(W–F) can be easily distinguished. The electron ionization mass spectrum of **6** showed the parent ion (m/z 653) with the expected isotopic pattern. The elemental analysis was compatible with structure **6**. The ^{19}F NMR spectrum of **6** consisted of a triplet and a doublet at 48.8 and −82.6 ppm, respectively, with ^{183}W satellite signals. This ^{19}F NMR spectral pattern is consistent with a trigonal-bipyramidal geometry around the metal center. The triplet appearing at the high field was assigned to the equatorial fluorine, and the doublet at the low field arises due to the axial fluorine atoms (see Experimental Section). The crystal structures of the chloro derivatives $\overline{NPPh_2NPPh_2NMCl_3}$ (M = Mo (**2**), W (**3**)) show a similar disposition of the chlorine atoms around the metal centers.[7,8] The $^{31}P\{^1H\}$ NMR spectrum of **6** exhibits a sharp singlet at 22.5 ppm.

Table I. ^{31}P NMR Spectroscopic Data[a]

compd	δ
$\overline{NPPh_2NPPh_2NMoCl_3}$[a] (**2**)	42.4 (s)
$\overline{NPPh_2NPPh_2NWCl_3}$[b] (**3**)	39.2 (s)
$\overline{NPPh_2NPPh_2NVCl_2}$ (**4**)	43.7 (s)
$\overline{NPPh_2NPPh_2NWBr_3}$ (**5**)	43.8 (s)
$\overline{NPPh_2NPPh_2NWF_3}$ (**6**)	22.5 (s)
$\overline{NPPh_2NPPh_2NReCl_4}$ (**7**)	46.2 (s)
$N_3P_3Ph_4Cl_2$[c]	17.2
$N_3P_3Ph_6$[c]	14.3

[a] Reference 7. [b] Reference 8. [c] Reference 12.

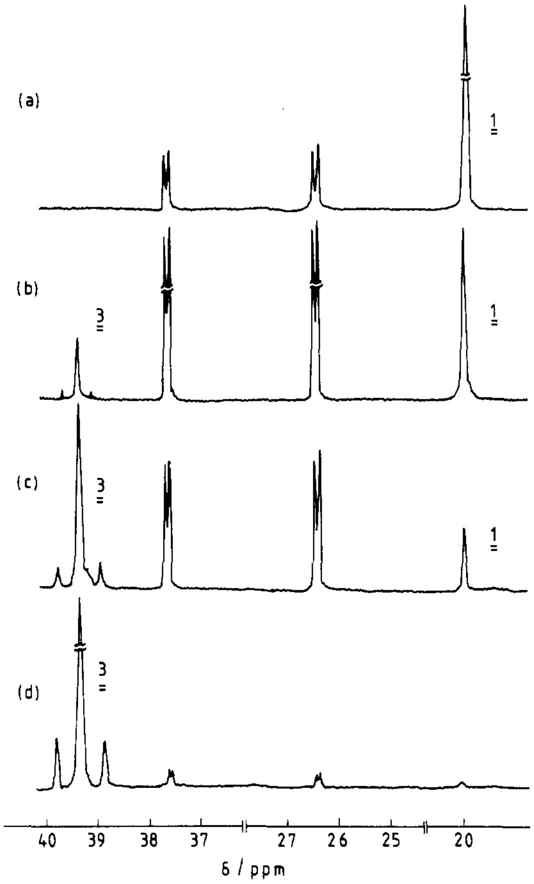

Figure 1. $^{31}P\{^1H\}$ NMR spectra obtained at different stages during the reaction of $[H_2NPPh_2NPPh_2NH_2]^+Cl^-$ (**1**), with WCl_6: (a) 1 h; (b) 4 h; (c) 8 h; (d) 24 h. The doublet signals between 26 and 38 ppm arise due to the unsymmetrically substituted WCl_6 salt of **1**; the signal due to cyclotungstaphosphazene (**3**) is shown with ^{183}W satellites [$^2J(^{183}W-^{31}P)$ = 63 Hz].

Synthesis and Characterization of $\overline{NPPh_2NPPh_2NReCl_4}$ (7). The reaction of **1** with $ReCl_5$ under chlorine atmosphere in CCl_4 medium at reflux conditions affords the cyclometallaphosphazene **7** in 60% yield. When this reaction was carried out in the absence of chlorine gas, instead of the cyclic compound, an acyclic metal halide–phosphazene salt seemed to result, as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum from this reaction mixture showed an AB spin pattern, indicating that $ReCl_5$ is substituted at only one of the NH_2 units in **1**. A longer reaction time has no significant effect on this product.

Compound **7** can be isolated as pink cubes after recrystallization from acetonitrile. Compound **7** is quite stable under a nitrogen atmosphere but decomposes slowly on exposure to air. It melts with decomposition at 190 °C.

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[11] Granger, P. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic: New York, 1983; Chapter 15, pp 385–417.

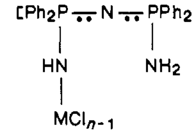
Inorg. Chem. **1987**, *26*, 4035–4039 **4035**

The infrared spectrum of **7** showed characteristic absorptions for P–N bonds between 1130 and 1270 cm^{-1}. The electron ionization mass spectrum for **7** consisted of the parent ion (m/z 739). The elemental analysis was compatible with structure **7**. The ^{1}H-decoupled ^{31}P NMR spectrum showed a single resonance line at 46.2 ppm.

The electron withdrawal property of transition-metal atoms causes a deshielding effect on the phosphorus chemical shifts of all the cyclometallaphosphazenes compared to the nonmetallated cyclophosphazene analogues (Table I).

Stability of Vanadium, Tungsten, and Rhenium in Their Highest Oxidation States. Compounds **4**–**7** provide examples of stable species of vanadium, tungsten, and rhenium in their highest oxidation state. It appears that the phosphazene skeleton has an ability to stabilize transition metals in their highest oxidation states.

Mechanism of the Formation of Cyclometallaphosphazenes. The interaction of the transition-metal halides MCl_n (VCl_4, $MoCl_5$, WCl_6, $ReCl_5$) with the linear phosphazene salt **1** appears to be a sequential process. The first step is the formation of an acyclic intermediate



followed by the subsequent cyclization step through the elimination of HCl. We have not isolated this acyclic intermediate; however, we have been able to monitor the progress of the reactions of the various metal halides with the linear phosphazene salt **1** by using $^{31}P\{^1H\}$ NMR spectroscopy. A typical series of spectra obtained for the reaction of WCl_6 with **1** at different reaction times are illustrated in Figure 1.

Conclusion

We have so far demonstrated that transition-metal atoms can be incorporated into sulfur–nitrogen[13] and phosphorus–nitrogen[7,8] ring skeletons through different synthetic strategies. The ready synthesis of these metallacycles has opened up a new topic of research in inorganic heterocyclic chemistry. The presence of metal–halogen bonds in compounds **2**–**7** offers opportunities for carrying out varieties of nucleophilic substitution reactions.

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Registry No. **3**, 101653-99-0; **4**, 110589-08-7; **5**, 110589-09-8; **6**, 110589-10-1; **7**, 110589-11-2.

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(12) Latscha, H. P. *Z. Anorg. Allg. Chem.* **1968**, *362*, 7.

(13) Roesky, H. W.; Anhaus, J.; Schmidt, H. G.; Sheldrick, G. M.; Noltemeyer, M. *J. Chem. Soc., Dalton Trans.* **1983**, *1207*.

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Ligand Isotopic Exchange of *cis*-Bis(acetylacetonato)dioxomolybdenum(VI) in Acetylacetone

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Received February 25, 1987

The ligand exchange of *cis*-bis(acetylacetonato)dioxomolybdenum(VI) in acetylacetone has been studied kinetically with the ^{14}C-labeling technique. The rate law was rate = $(k_1 + k_2[H_2O])$[complex] at 5.0, 15.0, 25.0, and 35.0 °C; k_1 and k_2 are 1.05 × 10^{-3} s^{-1} and 8.27 × 10^{-3} M^{-1} s^{-1} at 25 °C, respectively. $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are 64 ± 2 and 64 ± 1 kJ mol^{-1} and −86 ± 5 and −71 ± 4 J K^{-1} mol^{-1} for k_1 and k_2, respectively. Dilution of the solvent with acetonitrile and deuteriation of the acidic hydrogens of the solvent and of water decreased both rate constants. Application of pressure to the solution up to 92 MPa at 5 °C caused no significant change in the rate law, and the rates themselves, i.e. $\Delta V^\ddagger$'s, were ca. 0 cm^3 mol^{-1}. The mechanism of the reaction is discussed on the basis of these data.

Introduction

The kinetics of ligand substitution reactions of molybdenum(VI) complexes has been studied mainly in aqueous solution.[2-4] The participating species are not specified in some cases, since there are various molybdenum(VI) species, including dimers and polymers, in aqueous media depending on the pH and the concentration.[5] Anation and hydrolysis are sometimes accompanied by a change in the coordination number. Most aqua complex ions have oxide as an inert ligand and given regiospecificity on substitution.[4]

Some complexity may be ignored in the reactions in organic solvents. We have demonstrated the importance and usefulness of the solvent-exchange rate of the metal solvate involving bidentate ligands by the use of acetylacetonato complexes in acetylacetone (Hacac).[6,7] For Mo^{VI} complexes the solvent-exchange reactions in organic solvents have been less investigated, although a few reports have also been published on isotopic ^{18}O exchange between solvent water and MoO_4^{2-}.[8]

Molybdenum(VI) gives a discrete complex, *cis*-bis(acetylacetonato)dioxomolybdenum(VI), that is stable in dry organic solvents.[9] Craven et al.[10] investigated the intramolecular site

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(1) Present address: Natural Science Building, International Christian University, Osawa, Mitaka, Tokyo 181, Japan.

(2) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1–223.

(3) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1980.

(4) Saito, K.; Sasaki, Y. In *Advances in Inorganic and Bioinorganic Mechanisms*; Sykes, A. G., Ed.; Academic: London, 1982; Vol. 1, pp 179–216.

(5) Cruywagen, J. J.; Heyns, J. B. B.; Rohwer, E. F. C. H. *J. Inorg. Nucl. Chem.* **1978**, *40*, 53–59.

(6) Watanabe, A.; Kido, H.; Saito, K. *Inorg. Chem.* **1981**, *20*, 1107–1111 and references cited therein.

(7) Nagasawa, A.; Kido, H.; Hattori, T. M.; Saito, K. *Inorg. Chem.* **1986**, *25*, 4330–4333.

(8) (a) Hinch, G. D.; Wycoff, D. E.; Murmann, R. K. *Polyhedron* **1986**, *5*, 487–495. (b) Gamsjäger, H.; Murmann, R. K. In *Advances in Inorganic and Bioinorganic Mechanisms*; Sykes, A. G., Ed.; Academic: London, 1983; Vol. 2, pp 317–380.

(9) Fernelius, W. C.; Terada, K.; Bryant, B. E. *Inorg. Synth.* **1960**, *6*, 147–148.

(10) Craven, B. M.; Ramey, K. C.; Wise, W. B. *Inorg. Chem.* **1971**, *10*, 2626–2628. According to our recalculation from the data given in this reference, $\Delta S^\ddagger$ values therein should be corrected to −4.4 and −14 cal K^{-1} mol^{-1}, in benzene and in $CHCl_3$, respectively.

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