have a double Mo-Mo bond in the complex.[24] This is to be compared to the weak interaction proposed by Dahl in the complex $(\pi\text{-}C_5H_5MoOS)_2$ and the strong bond suggested by Drew's results.

The rest of the molecule, namely, the dithiocarbamato ligand and the propyl chains of both ligands, present the usual geometries and bond lengths taking into account some imprecision of carbon-carbon bond lengths. This may result from the strong thermal motions of these atoms. As shown in Figure 3, the crystal cohesion is mainly ensured by contacts between the propyl chains and there are only weak interactions between the molecules. This may be responsible for some lack of precision in the resolution of the structure at the level of the propyl chains.

Registry No. $[MoS(SCN(C_3H_7)_2)(S_2CN(C_3H_7)_2)]_2$, 40631-71-8.

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[24] The Mo-S_1 bond order is probably more than 1.0. If we use, as Drew suggests, an Mo-S_1 bond order of 1.5, bond orders of 1.0 for all other sulfurs, and a bond order of 1.5 for Mo-C_1, we get a bond order of 1 for the thiocarboxamido complex. However, the value of 1.5 for the Mo-S_1 bond order is probably overestimated. A value of 1.3, similar to that suggested by Cotton[25] in the Mo_2O_2 system, seems more reasonable and leads to essentially the same results as above.

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Notes

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Phenylimino Quaternization of Birdcage Phosphorus Compounds

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One of the less explored areas of phosphorus chemistry consists of the broad group of structures[2-4] in which each phosphorus atom is bonded only to nitrogen atoms. This group has received relatively little attention as compared to the massive body of work[4,5] on the compounds in which each phosphorus is bonded only to oxygen atoms. In the study reported here, a series of birdcage structures is described in which four phosphorus atoms are bridged by nitrogen and each tetracoordinate phosphorus is surrounded by four nitrogen atoms. Some related chemistry is also discussed.

Experimental Section

Materials. Due to the sensitivity of the compounds to moisture and oxygen, all operations were carried out under dry nitrogen, with exclusion of light for P_4O_6 and its reaction products. The solvents were of Spectrograde quality and practically water free; prior to use they were saturated with dry nitrogen. High-purity tetraphosphorus hexaoxide was purchased from Albright & Wilson, Ltd., London, England, and tetraphosphorus hexamethylhexaimide was prepared by an improvement to the procedure given in ref 6. Phenyl azide was made according to the literature.[7]

Analyses. The ^{31}P nuclear magnetic resonance (nmr) spectra were run on a Varian XL-100-15 spectrometer at 40.55 MHz, with locking onto the deuterium resonance of D_2O which was contained in a 5-mm tube that was concentrically inserted into the 12-mm tube holding the sample. Broad-band decouplings of the protons were employed and chemical shifts are reported *vs.* external 85% H_3PO_4. The ^1H nmr spectra were obtained with a Varian A-60 spectrometer in $CDCl_3$ solution with tetramethylsilane as the internal-reference standard. Elemental analyses were carried out by Chemalytics, Inc., Tempe, Ariz. Uncorrected melting points were obtained in sealed capillaries on a Mel-Temp unit.

Reactions. Sufficient birdcage compound $[P_4(NCH_3)_6$ or $P_4O_6]$ was dissolved in 10 ml of benzene to make a *ca.* 1.0 *M* solution and the desired amount of phenyl azide was pipetted in from a 3.5 *M* solution in benzene.

Isolation of Crystalline Species. The two compounds corresponding to one and four phenylimino groups being bonded to the tetraphosphorus hexamethylhexaimide birdcage molecule have been isolated in crystalline form. The first of these compounds, which might be named hexa-μ-methylimino-tetraphosphorus monophenylimide, was prepared by adding 1.88 g of $C_6H_5N_3$ in 10 ml of hexane to a solution of 4.70 g of $P_4(NCH_3)_6$ in 20 ml of hexane. Since $[P_4(NCH_3)_6]NC_6H_5$ is insoluble in hexane, a yellow precipitate formed within a few seconds, as would be predicted from the value presented for k_1 of eq 1. After stirring for 10 min, the resulting yellow crystals were filtered within a drybox and dried under vacuum; yield 4.88 g (61%); mp 96.5° dec. *Anal.* Calcd for $C_{12}H_{23}N_7P_4$: C, 37.03; H, 5.95; N, 25.19; P, 31.83. Found: C, 37.37; H, 5.66; N, 25.30; P, 31.29. The ^{31}P nmr data are presented in Table I and the ^1H data are the following: $\tau(C_6H_5)$ 2.58 (complex multiplet, 5 H), $\tau(CH_3)$ *ca.* 6.9 (middle of complex multiplet, 18 H).

The preparation of $[P_4(NCH_3)_6](NC_6H_5)_4$ was accomplished by adding 2.32 g of $C_6H_5N_3$ in 10 ml of benzene to a solution consisting of 1.5 g of $P_4(NCH_3)_6$ in 5 ml of benzene. After gentle reflux for 20 hr and then concentration to a total volume of about 7 ml, a yield was obtained of 1.1 g (34% of theory) of white crystals, mp 167°, which were filtered and dried under vacuum. *Anal.* Calcd for $C_{30}H_{38}N_{10}P_4$: C, 54.46; H, 5.79; N, 21.17; P, 18.72. Found: C, 54.58; H, 5.96; N, 20.91; P, 18.56. Again the ^{31}P nmr data for this compound are presented in Table I and the ^1H data are as follows: $\tau(C_6H_5)$ 3.00 (complex multiplet, 20 H); $\tau(CH_3)$ 6.82 (pseudotriplet, 18 H); $J(PNCH_3) = 10.3$ Hz.

Attempts to make the compounds $[P_4(NCH_3)_6](NC_6H_5)_2$ and $[P_4(NCH_3)_6](NC_6H_5)_3$ led to the formation of oily products which we were unable to crystallize. As can be seen from the kinetic calculations, the rate constants for the reactions of eq 1-4 are such that only $[P_4(NCH_3)_6](NC_6H_5)$ and the final product $[P_4(NCH_3)_6](NC_6H_5)_4$ can be made essentially pure. Presumably, the presence of some of the neighboring species of this series of compounds inhibits the crystallization of the two intermediate structures.

Results and Discussion

Quaternization of $P_4(NCH_3)_6$. When increasing amounts of phenyl azide are added at 40° to tetraphosphorus hexamethylhexaimide in a nonreactive organic solvent (benzene), periodic observation by ^{31}P nuclear magnetic resonance (nmr) shows that there is a stepwise addition of phenylimino groups

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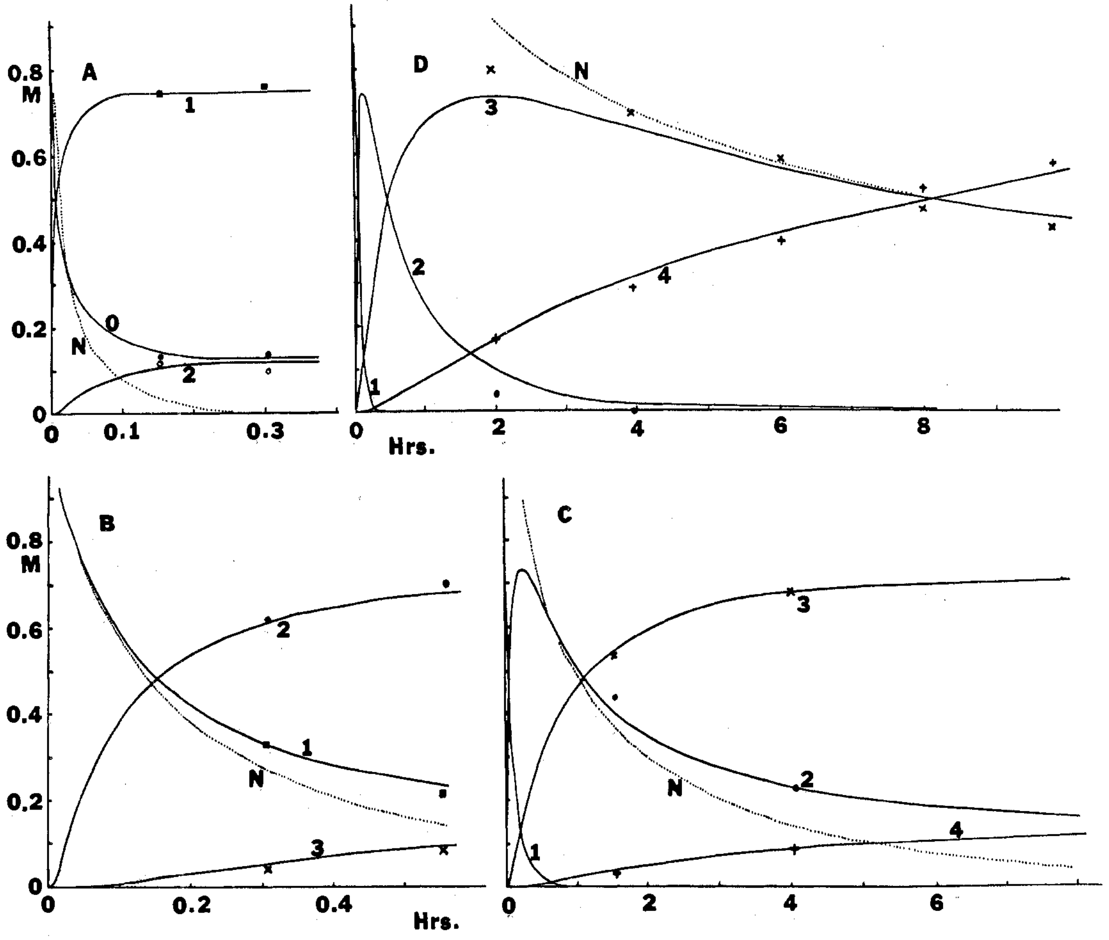

Figure 1. The rate plots for the reaction between tetraphosphorus hexamethylhexamide and phenyl azide at 40°. The numbers ranging from 0 through 4 on the curves indicate the value of n for the particular product $[P_4(NCH_3)_6](NC_6H_5)_n$. The graphs correspond to the following starting compositions: $[C_6H_5N_3]/[P_4(NCH_3)_6]$ = 1.00 for A, 2.00 for B, 3.00 for C, and 4.00 for D. The symbol N on the dotted curve stands for phenyl azide and this curve was calculated but not measured.

Table I. ^{31}P Chemical Shift and P-P Coupling Constants[a]

	δ_P, ppm	δ_{P^*},[b] ppm	Pattern[c] (P, P*)	Ratio (P:P*)	J_{PP^*}, Hz
$P_4(NCH_3)_6$	−81.9		s	4:0	
$P_4(NCH_3)_6(NC_6H_5)$	−123.1	−8.7	d, q	3:1	11.8 ± 0.3
$P_4(NCH_3)_6(NC_6H_5)_2$	−140.1	+3.2	t, t	2:2	24.5 ± 0.2
$P_4(NCH_3)_6(NC_6H_5)_3$	−81.2	+2.1	q, d	1:3	36.7 ± 0.3
$PR(NCH_3)_6(NC_6H_5)_4$		+13.4	s	0:4	

[a] Measurements carried out on benzene solutions. [b] P* denotes the "oxidized" phosphorus. [c] Upon decoupling all the hydrogens.

to the $P_4(NCH_3)_6$ molecule (*via* the Staudinger reaction[8]). The nmr parameters observed in such a study are presented in Table I, from which it can be seen that the chemical shifts and the first-order splitting patterns observed with broadband proton irradiation prove the structures of the different species resulting from successive addition of the phenylimino group to the phosphorus atoms of the $P_4(NCH_3)_6$ molecule. Thus, a downfield singlet is observed for $P_4(NCH_3)_6$, as would be expected for all four of the phosphorus atoms exhibiting an unshared pair of electrons. Addition of a phenylimino group to one of these four phosphorus atoms leads to a quartet corresponding to this phosphorus which exhibits one-third the area of the doublet corresponding to the three remaining phosphorus atoms. The quartet appears in the spectral region near the reference peak of 85% phosphoric acid; whereas the doublet is about 100 ppm downfield in the spectral region for such triply connected phosphorus atoms. When two of the phosphorus atoms of $P_4(NCH_3)_6$ have each acquired a phenylimino group, there is a pair of triplets of equal area, one in the 0-ppm region and one in the −100-ppm region. Likewise, three phenylimino groups on the $P_4(NCH_3)_6$ molecule leads to a downfield quartet having a third the area of a doublet in the region near 0 ppm. Finally, the donation of a phenylimino group to all four of the phosphorus atoms of $P_4(NCH_3)_6$ leads to a singlet in the zero-shift region.

In all of the various preparations involved in this study, the ^{31}P nmr peaks ascribed to each molecule in Table I were found consistently to exhibit the theoretical area ratios, so that during a reaction sequence the sets of resonances ascribed to the various molecules were seen to vary in such a way that each set must necessarily be due to a singlet chemical structure. The ^{31}P chemical shifts assigned in Table I to the phosphorus atom having four nearest-neighbor nitrogen atoms are undoubtedly correct, as indicated by the value of −14 ppm reported[9] for the shift of the related compound $C_6H_5NP[N(C_2H_4)_2]_3$.

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(8) For a comprehensive review up to 1966 on this reaction, see G. Singh and H. Zimmer, *Organometal. Chem. Rev., Sect. A*, 2, 279 (1967).

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The rates of formation of the various molecules in benzene solution at 40° was the subject of a computer analysis based on the set of four equations[10]

$$P_4(NCH_3)_6 + C_6H_5N_3 \xrightarrow{k_1} C_6H_5N[P_4(NCH_3)_6] + N_2 \qquad (1)$$

$$C_6H_5N[P_4(NCH_3)_6] + C_6H_5N_3 \xrightarrow{k_2} (C_6H_5N)_2[P_4(NCH_3)_6] + N_2 \qquad (2)$$

$$(C_6H_5N)_2[P_4(NCH_3)_6] + C_6H_5N_3 \xrightarrow{k_3} (C_6H_5N)_3[P_4(NCH_3)_6] + N_2 \qquad (3)$$

$$(C_6H_5N)_3[P_4(NCH_3)_6] + C_6H_5N_3 \xrightarrow{k_4} (C_6H_5N)_4[P_4(NCH_3)_6] + N_2 \qquad (4)$$

Curve fitting of the experimental data, assuming that each reaction is first order in each reagent, leads to the following values for the rate constants: $k_1 \geqslant 50$, $k_2 = 7$, $k_3 = 1.0$, $k_4 = 0.3\ M^{-1}\ \text{hr}^{-1}$. The curves calculated from these rate constants for 1:1, 1:2, 1:3, and 1:4 mole ratios of tetraphosphorus hexamethylhexaimide to phenyl azide are shown in Figure 1.

Quaternization of Other Birdcage Molecules. When various proportions of tetraphosphorus hexaoxide (^{31}P chemical shift of −113.5 ppm) and phenyl azide were mixed together in benzene or methylene chloride, with and without exclusion of light and heating up to 40° for several hours, the only cage-substitution compound which was obtained was the monosubstituted product $P_4O_6(NC_6H_5)$. In addition, there were soluble decomposition products and some of the yellowish white amorphous material which was previously described[11] as being a high polymeric form of P_2O_3 with occasional end groups.

The ^{31}P nmr pattern of $P_4O_6(NC_6H_5)$ in benzene solution consisted of a doublet at −140.6 ppm which exhibited 3 times the peak area of the first-order quartet at +42.7 ppm. J_{PP^*} was found to equal 4.4 ± 0.1 Hz. Again, the consistent-area relationship of these peaks in various reaction-product mixtures showed that they belong to a single molecule.

Attempts to prepare phenylimino-substitution products from phosphorus sesquisulfide, P_4S_3, and from white phosphorus, P_4, resulted in failure. In both cases there was no sign of reaction or even of decomposition upon boiling the appropriate carbon disulfide solutions at atmospheric pressure for as long as 6 hr.

Registry No. $[P_4(NCH_3)_6]NC_6H_5$, 39937-16-1; $[P_4(NCH_3)_6](NC_6H_5)_4$, 39937-17-2; $P_4(NCH_3)_6$, 10369-17-2; $P_4(NCH_3)_6(NC_6H_5)_2$, 39937-18-3; $P_4(NCH_3)_6(NC_6H_5)_3$, 40031-97-8; P_4O_6, 12440-00-5; $C_6H_5N_3$, 622-37-7.

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Kinetics of the Dissociation of Binuclear Oxygen-Bridged Complexes of Iron(III) with 1,10-Phenanthroline and 2,2′-Bipyridine

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The binuclear oxygen-bridged complexes of iron(III) with 1,10-phenanthroline and 2,2′-bipyridine, $Fe_2OL_4Cl_4$ (L = phen or bipy), are high-spin complexes with a linear Fe-O-Fe "bridge."[1-6] While they have the structure $[L_2ClFe\text{-}O\text{-}FeClL_2]^{2+}$ in the solid,[3] dissolution in water effects rapid replacement of coordinated chloride ligands by water molecules.[7] Hence, an aqueous solution of the complex is best represented as $[L_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)L_2]^{4+}$.[7] While aqueous solutions of these complexes are indefinitely stable in the dark (they undergo photoreduction on ultraviolet irradiation[7]), they dissociate in acid solutions with complete loss of color. The present work deals with the kinetics of the dissociation of $[L_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)L_2]^{4+}$ complexes in dilute nitric acid solutions.

Experimental Section

Materials. The binuclear iron(III) complexes $Fe_2(phen)_4OCl_4$ (hereafter called "DP") and $Fe_2(bipy)_4OCl_4$ (hereafter called "DB") were prepared by literature procedures.[7c,8,9] Water was purified by distillation from potassium permanganate. Reagent grade 1,10-phenanthroline and 2,2′-bipyridine (E. Merck) were purified by recrystallization from aqueous ethanol.[10] All other chemicals were reagent grade and were used without further purification.

Kinetic Runs. The compounds DP and DB have charge-transfer absorption maxima at 28,570 cm^{-1} (ϵ_{max} 9.20 × 10^3 l. mol^{-1} cm^{-1}) and 29,000 cm^{-1} (ϵ_{max} 7.40 × 10^3 l. mol^{-1} cm^{-1}), respectively. These charge-transfer bands were destroyed during the acid dissociation. A spectrophotometric method was used to follow changes in absorbance at the charge-transfer band during dissociation. The products of the dissociation, aquoiron(III) and protonated bipyridine, have very little absorbance in the 28,000–29,000-cm^{-1} region (ϵ ~60 for aquoiron(III) and ~75 for protonated bipyridine), and, hence, the absorption due to aquoiron(III) and protonated bipyridine is negligible at the 10^{-4} *M* concentrations of the complex used. The protonated phenanthroline has significant absorbance in this region (ϵ for phenH$^+$ at 28,570 cm^{-1} is 800) and hence, was taken into account in calculating the decrease in absorbance during the acid dissociation of DP.

Absorbance changes were recorded on a Unicam SP 700 spectrometer. Suitable volumes of standard aqueous solutions of the complex, sodium nitrate (used to adjust the ionic strength), and nitric acid were mixed rapidly and transferred to a 1-cm quartz cell. The time elapsed between the mixing of the solutions and starting to record the absorbance was 1 min. The spectrometric cell compartments were thermostated at the required temperature

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