Mechanism i, although possible on energetic grounds if the excited state is a typical porphyrin one,[35] is implausible owing to the presumably very short lifetime of the excited states of iron(III) porphyrin complexes in fluid solution.[4] Moreover, this mechanism is clearly ruled out by the strong wavelength dependence of the quantum yields (Table I), which is at odds with the wavelength-independent behavior of metalloporphyrin luminescence.[4]

As far as mechanisms ii, iii, and iv are concerned, discrimination among the three may prove difficult on experimental grounds. In fact all three require light absorption into specific LMCT bands. All these mechanisms imply dependence on type as well as concentration of the alcohols: mechanism iii through complex formation equilibrium and mechanisms ii and iv through the scavenger content of the solvent cage surrounding the complex (note that the scavenging occurs over an alcohol concentration range much higher than that involved in typical bulk solution scavenging phenomena). The fact that no transient absorbance change can be observed in the absence of alcohols cannot be taken as evidence for mechanism iii since the same result would be expected if the scavenging process of mechanisms ii and iv is to occur in the solvent cage, i.e., in a time scale much shorter than the time resolution of the flash experiments.

As far as the wavelength dependence of the photoreduction quantum yield is concerned, it might be remarked that the photoreduction is only relatively efficient at $\lambda \leq 400$ nm. This implies light absorption into specific electronic absorption bands, which according to mechanisms ii–iv should be of the LMCT type. It can be noticed that the OH → Fe(III) LMCT band in Fe-$(H_2O)_5OH^{2+}$ is found at about 300 nm.[34] Considering the lowering in redox potentials obtained in going from the aqueous ion (+0.77 V) to the porphyrin complex (−0.15 V), it might be expected that OH → Fe(III) LMCT bands should lie at wavelengths substantially lower than 300 nm in $Fe^{III}PP(py)(OH)$. Porphyrin complexes containing coordinated alkoxy groups or pyridine (which are more oxidizable than OH^-) would, on the other hand, exhibit R_1R_2CHO → Fe(III) or py → Fe(III) LMCT bands at higher wavelengths. Thus, although no clear-cut decision can be made among mechanisms ii–iv for the primary photoredox process, this argument tends to favor the direct intramolecular electron-transfer mechanism from the coordinated alkoxy group (mechanism iii) or pyridine (mechanism ii) to the metal.[37] The explanation of the much lower primary photoreduction efficiency of *tert*-butyl alcohol relative to the other alcohols (Figure 4) cannot be based on the redox properties of the alcohols (Table II) but rather must involve the low ability of *tert*-butyl alcohol to either coordinate to (mechanism iii) or solvate (mechanism ii) the Fe(III) complex. Figure 1 shows that *tert*-butyl alcohol is by far less effective than the other alcohols in modifying the spectrum of the complex, a feature which supports the above considerations.

As a final comment, it may be noticed that the photochemistry of metal porphyrin complexes is often considered as that of typical porphyrin chromophores, which are modified by the presence of the metal to the extent to which it affects the lifetimes or interconversion efficiencies of the porphyrin excited states. In contrast to this oversimplified view, the results reported in the present paper show that for some metal porphyrin complexes the photochemistry may be entirely determined by specific, high-energy excited states of the whole molecular system.

Acknowledgment. We thank Dr. C. Chiorboli for his kind assistance in performing the gas chromatographic analyses.

(35) Energies of metalloporphyrin triplet excited states are typically at about 43 kcal/mol (1.87 eV).[4] Given the ground-state redox potential (−0.15 V),[1] it is possible to calculate[31] an excited state reduction potential of about 1.7 V for $Fe^{III}PP(py)(OH)$. In view of the one-electron redox potentials of the alcohols used (Table II) and of pyridine (1.82 V in CH_3CN vs. Ag/Ag^+),[36] the one-electron oxidation of alcohols and pyridine by the excited complex seems to be thermodynamically allowed.

(36) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous systems"; Marcel Dekker: New York, 1970.

(37) While both mechanisms are plausible in this solvent system, it should be noted that qualitatively identical results, i.e., photoreduction of Fe(III) to Fe(II) complex, can be obtained in the absence of pyridine, albeit with poor quantitative reproducibility.

Some Caged Oxyazaphosphoranes

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Abstract: 2,8-Dimethyl-2,5,8-triaza-1-phosphabicyclo[3.3.0]octane (**9**) has been prepared as an extremely unstable monomer. This monomer on standing polymerizes rapidly and reversibly. The monomer has been allowed to react with biacetyl and benzil to give the mixed oxyazaphosphoranes **13** and **14**. Variable-temperature ^{13}C NMR studies show that these materials do not undergo rapid intramolecular ligand reorganization nor do they undergo rapid intermolecular reorganization. In the case of **14** it remains rigid up to 95 °C. 2,10-Dimethyl-2,6,10-triaza-1-phosphabicyclo[4.4.0]decane (**16**) has been prepared and found to be much more stable than **11** toward polymerization. Condensation of **16** with benzil yields a phosphorane, **17**. This material undergoes rapid intramolecular ligand reorganization at room temperature. Variable-temperature ^{13}C NMR studies show that this process has a free energy of activation of 13 kcal/mol with a coalescence temperature of −7 °C. These findings further delineate those factors which control rates of intramolecular ligand reorganization of phosphoranes, and they impose limitations on various proposed mechanisms.

Although the chemistry of phosphoranes has developed rapidly during the past two decades, there are still a number of interesting questions which must be answered before a satisfying understanding of the chemistry of these molecules can be achieved. Some of these questions are as follows: what are the favored structures where the gamut runs from trigonal bipyramidal (TBP) to square or rectangular pyramidal (SP or RP); what factors govern the ligand placement in these structures, i.e., apical (a) or equatorial (e) in a TBP or basal (b) or apical (a) in SP or RP; how do the rates of intramolecular ligand reorganization vary as

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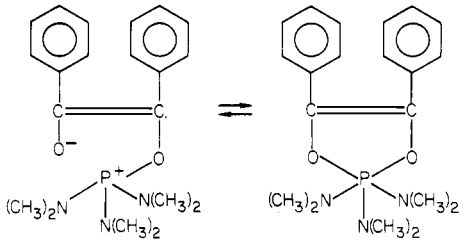
a function of ligand structure and phosphorane structure.[1] In a general way considerable progress has been made in these various areas; the major problem has arisen because of attempts to over generalize. For example, statements can be found in abundance that five-membered rings never adopt a diequatorial disposition. This is simply not true. Similarly there has been considerable confusion concerning the structures of these materials and many workers have only considered TBP geometries, a practice which has led to several misinterpretations of important structural data.[2]

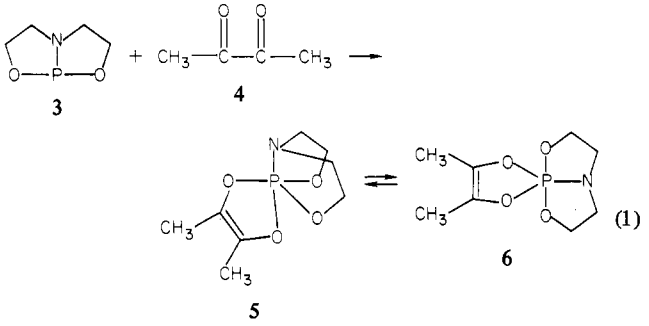
The work to be reported here concerns itself with several mixed oxyazaphosphoranes, a class of compounds which has received much less attention than the oxyphosphoranes. The chemistry of some mixed oxyazaphosphoranes was first investigated by Ramirez and his co-workers.[3] They found that various tris(dialkylamino)phosphines will condense with α-diketones such as phenanthrenequinone or benzil to give adducts which often exist as phosphoranes or in some cases as a dipolar ion. Compounds **1** and **2** are interesting examples. These substances can be isolated



1 **2**

in a crystalline form, **1**, or alternatively as **2**, and in solution both structures are in equilibrium with each other.

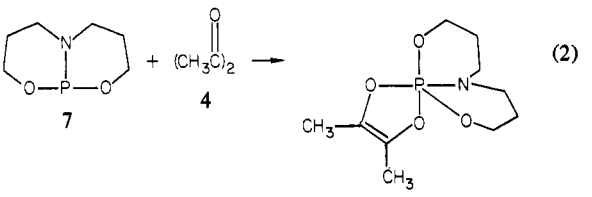
Recently the unique compound **3** was prepared, and some of its chemistry was elucidated.[4] A number of phosphoranes have been prepared from **3** (see eq 1).[5] One of the more interesting



3 **4** **5** **6** (1)

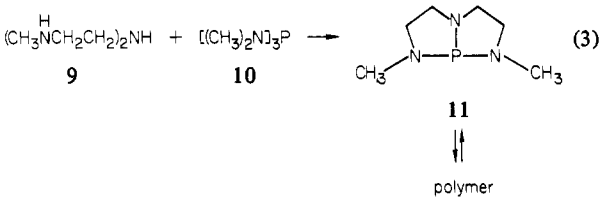
developments was the finding that **5** and other related phosphoranes derived from **3** undergo intramolecular ligand reorganization and that **6** with a diequatorial five-membered ring is formed as a transition state or intermediate. On being cooled **5** is found to be the favored structure, and intramolecular ligand reorganization is inhibited.

Compound **8** was also prepared by condensation of **7** with biacetyl (eq 2). It was found that **8** undergoes rapid intramolecular ligand reorganization at room temperature and that this process can be inhibited sufficiently on cooling so that separate resonances for most of the various carbons can be observed. The spectra indicate that **8** is the favored structure and that a structure analogous to **6** is not involved in the ligand reorganization process over the temperature range studied.



7 **4** **8** (2)

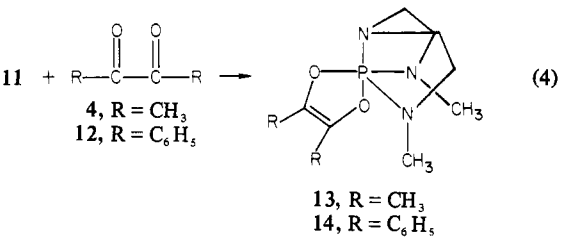
It seemed of some interest to prepare all nitrogen-containing analogues of **3** and **7** and to study phosphoranes derived from them. The triamine **9** was prepared by conventional procedures which can be found in the Experimental Section. Condensation of **9** with **10** followed by distillation yielded a mobile liquid which rapidly turned to a gummy solid (see eq 3). This latter material



9 **10** **11** polymer (3)

is undoubtedly a polymer.[6] Heating the polymer in vacuo led to the distillation of **11** in virtually quantitative yield, and thus **11** can be regenerated and its reactions can be studied if it is used immediately after distillation. In some cases it was distilled directly into the reactants which were maintained at low temperatures.

Attempts to convert **11** into a variety of phosphoranes by using standard reagents were not successful. In general, **11** was converted into a polymer. Condensation of **11** with biacetyl (**4**) and benzil (**12**) did yield phosphoranes as evidenced by their ^{1}H, ^{13}C, and ^{31}P NMR spectra (see eq 4). Compound **13**, the product



4, R = CH_3
12, R = C_6H_5
13, R = CH_3
14, R = C_6H_5 (4)

from biacetyl, was found to be unstable above 0 °C. There was no change in the ^{13}C NMR spectrum up to this temperature. On the other hand, **14** was isolated as a crytalline solid and it was stable in solution at 95 °C. This striking difference in stability of biacetyl and benzil adducts for compounds containing at least one nitrogen bonded to phosphorus seems quite general. For example, the adduct from benzil and hexamethylphosphorous triamide is stable at room temperature for several days, whereas that from biacetyl decomposes on warming to room temperature. Compounds **6** and **8** are considerably less stable than the benzil adducts. Several other similar cases have been found in other investigations. Both **13** and **14** have ^{13}C NMR spectra which show that the olefinic carbons of the five-membered rings are nonequivalent. In the case of **13** the methyl group carbons are also nonequivalent as are the ipso carbons of the aromatic rings of **14**. These data are of course in agreement with the static trigonal-bipyramidal structures illustrated. There are square-pyramidal structures which also satisfy these data. They are much more strained than the TBP structures, and there does not seem to be any reason for considering them. The barrier to ligand reorganization which would render the various carbons equivalent must be reasonably high. A solution of **14** at 95 °C still showed nonequivalent olefinic and ipso carbons. From other data[5,7] it is possible to suggest that the barrier is at least 15 kcal/mol and

(1) (a) Emsley, J.; Hall, C. D. "The Chemistry of Phosphorus"; Wiley: New York, 1976; Chapter 6. (b) Sheldrick, W. S. *Top. Curr. Chem.* **1978**, *73*, 1–49. (c) Lukenbach, R. "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements"; G. Theime: Stuttgart, 1973.

(2) For a recent review see: Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.

(3) Ramirez, F. *Acc. Chem. Res.* **1968**, *1*, 168.

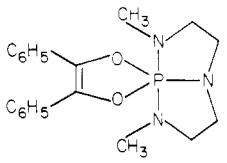
(4) Houalla, D.; Osman, F. H.; Sanchez, M.; Wolf, R. *Tetrahedron Lett.* **1977**, 3041.

(5) Denney, D. B.; Denney, D. Z.; Hammond, P. J.; Tseng, K.; Huang, C.; *J. Am. Chem. Soc.* **1980**, *102*, 5073.

(6) Atkins, T. J. U.S. Patent 3 996 276, 1976.

(7) Campbell, B. S.; De'Ath, N. J.; Denney, D. B.; Denney, D. Z.; Kipnis, I. S.; Min, T. B. *J. Am. Chem. Soc.* **1976**, *98*, 2924.

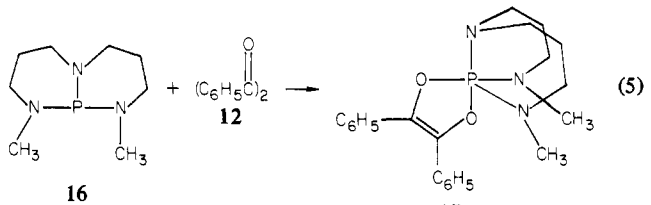
probably somewhat more. If **14** were to undergo intramolecular ligand reorganization by the Berry mechanism,[8] a structure **15**



15

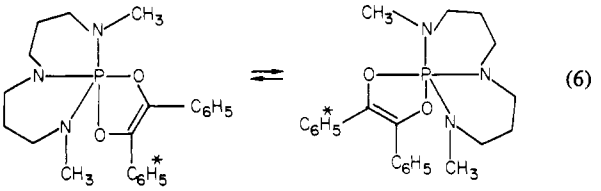
analogous to **6** could be formed as a transition state or intermediate. The difference in energy required to form **15** as compared to **6** should be considerable. In the case of **6** the nitrogen enters an equatorial position which is favored over an oxygen[9] and two oxygens enter apical positions as compared to one in **5**. These factors tend to overcome the energy required to place the five-membered ring diequatorial. In the case of **14** interconverting to **15** there is no such balancing of energies. In fact two nitrogens that are equatorial in **14** are replaced by only one in **15**. Similarly there are no apical oxygens in **15** as compared to one in **14**. Clearly in the conversion of **14** to **15** there are no offsetting energy changes and thus the activation energy for interconversion is increased over that required for the **5** to **6** interconversion. An alternate ligand reorganization by the Berry mechanism will be considered later.

Compound **16** has also been prepared, and unlike **11**, it has been found to be reasonably stable toward polymerization (see eq 5).



16 **17** (5)

The condensation product of **16** and benzil has ^1H, ^{13}C, and ^{31}P NMR spectra which indicate that it is a phosphorane. The ^{13}C NMR spectrum at room temperature shows that the two olefinic carbons of the five-membered ring are equivalent with weak coupling to phosphorus and that the ipso carbons of the phenyl groups are equivalent with J_{POCC} = 10.6 Hz. Other potentially equivalent carbons are found to be so. The observation of coupling shows that ionization–recombination cannot be responsible for the equivalency of the carbons. On cooling of the solution, the ^{13}C NMR spectrum becomes much more complex, and at −55 °C two ipso carbons, J_{POCC} = 9.9 Hz and J_{POCC} = 11.4 Hz, are found. The pairs of carbons of the six-membered ring system remain equivalent as do the methyl group carbons. Clearly these data can be explained by an intramolecular ligand reorganization process. The free energy of activation for this rearrangement is 13 kcal/mol, with a coalescence temperature of −7 °C. There are several ways in which this reorganization could occur. A structure analogous to **6** accounts for the ambient ^{13}C NMR spectrum. The ambient ^1H NMR spectrum at 60 MHz is extremely complex in the aliphatic region. The absorptions of the hydrogens of the methyl groups are easily recognized. The remainder is not that which one might expect for the C_{2v} structure analogous to **6**. The ^1H NMR spectrum argues against the formation of the C_{2v} structure as an intermediate or transition state. Such a structure will be of high energy because the five-membered ring adopts a diequatorial disposition. The NMR data can be explained without invoking this high-energy structure, and thus it will not receive further consideration. A particularly satisfying explanation of the NMR data is found if **17** is considered to be the low-energy form. In this conformer the olefinic and ipso carbons are nonequivalent whereas the pairs of methylene carbons are equivalent which is precisely what is found. The ambient ^{13}C NMR spectrum is arrived at if **17** can convert into **18a** and **18b** (enantiomers) which then must interconvert. The relatively high activation energy for the process is most probably associated with the **17** to **18a** and **18b** interconversion rather than the **18a** ⇄ **18b** equilibrium. Tripett[10] and his co-workers have shown that there



18a **18b** (6)

is a highly preferred orientation of a nitrogen in an equatorial position of a phosphorane. Such a nitrogen is sp^2 hybridized, and the p orbital containing the lone pair lies in the equatorial plane. When the nitrogen is part of a six-membered ring, this orientation is achieved with an equatorial–apical ring which is in the boat conformation. A model of **17** shows clearly that the two rings can adopt boat conformations and that the equatorial nitrogens when sp^2 hybridized have the p orbitals in the plane of the ring. A model of **18** shows that to achieve this orientation requires considerable twisting. The activation energy for the interconversion of **17** → **18** must certainly include the different orientations of the lone pairs in the two conformers. Returning to **14**, it is clear that it does not undergo an interconversion into structures similar to **18a** and **18b** because of the necessity of placing a five-membered dinitrogen-containing ring diequatorial.

It is interesting to consider the alternate mechanism for intramolecular ligand reorganization, i.e., the "Turnstile Rotation Mechanism" and its variants. The multiple "Turnstile Rotation Mechanism" was suggested as a means by which compounds similar to **5**, **13**, and **14** could undergo intramolecular ligand reorganization without forming structures such as **6** and **15**. It seems increasingly clear that those constraints which govern the Berry mechanism must also govern multiple TR processes even though they were suggested as a means of by-passing higher energy structures such as **6** and **15**.[10]

Experimental Section

^1H NMR spectra were run on Varian Model T-60 and FT-80 spectrometers. All chemical shifts are reported in parts per million relative to internal tetramethylsilane. ^{13}C and ^{31}P NMR spectra were run on a Varian Model FT-80 spectrometer equipped with a 10-mm, variable-temperature, broad-band probe. All ^{31}P chemical shifts are reported in parts per million relative to external 85% phosphoric acid (downfield shifts are positive) and all ^{13}C chemical shifts are reported in parts per million relative to internal tetramethylsilane. In all cases the ^{13}C spectra were obtained by using full proton decoupling, a 30° flip angle and a 2-s repetition rate with no pulse delay.

Preparation of Tris(*p*-toluenesulfonyl)-β,β′-diaminodiethylamine. A mixture of 51.6 g (0.5 mol) of diethylenetriamine and 300.0 g (1.57 mol) of *p*-toluenesulfonyl chloride in 400 mL of pyridine was heated at 80 °C under nitrogen for 1 h. The hot reaction mixture was added to 300 mL of water, 100 g of ice, and 400 mL of concentrated hydrochloric acid. The product was filtered, washed with water, and dried to give 200 g (71%) of the triamide, mp 176–177 °C (lit.[10] 173 °C).

Preparation of *N,N″*-Dimethyltris(*p*-toluenesulfonyl)-β,β′-diaminodiethylamine. A mixture of the triamide, (200 g, 0.35 mol), 45 g (0.80 mol) of potassium hydroxide, and 500 mL of 95% ethanol was heated under reflux with stirring. After the mixture became homogeneous, 99.5 g (0.79 mol) of dimethyl sulfate was added. After being heated for 30 min, the mixture was cooled and the product was isolated by filtration. The product was washed several times with ethanol and water and then dried to give 203 g (97%) of material, mp 152–154 °C (lit.[11] 152–153.5 °C).

Preparation of *N,N″*-Dimethyldiethylenetriamine. A mixture of the triamide (202 g, 0.34 mol) and 110 mL of concentrated sulfuric acid was heated with stirring to ca. 100 °C. Water was cautiously added dropwise

(8) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.
(9) (a) De Bruin, K. E.; Padilla, A. G.; Campbell, M. I. *J. Am. Chem. Soc.* **1973**, *95*, 4681. (b) Oram, R. K.; Trippett, S. *J. Chem. Soc., Perkin Trans.* **1973**, 1300.
(10) Ramirez, F.; Ugi, I. *Bull. Soc. Chim. Fr.*, **1974**, 453.
(11) Bone, S. A.; Tripett, S.; Whittle, P. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 80.

and very slowly. When the reaction mixture remained homogeneous after the addition of water, it was cooled to 70 °C and slowly neutralized by adding sodium carbonate and water. After the mixture became strongly basic, the water was removed in vacuo and by azeotropic removal with benzene. The solids were washed with benzene which was evaporated to give a liquid which was distilled (bp 204–207 °C) to yield 11.8 g (27%) of product; ^{1}H NMR (neat) δ 1.55 (s, 3 H), 2.35 (s, 6 H), 2.65 (s, 8 H).

Preparation of 11. To a stirred solution of 11.5 g (87.6 mmol) of *N,N″*-dimethyldiethylenetriamine in 250 mL of toluene, heated under reflux, was added dropwise 14.3 g (87.6 mmol) of hexamethylphosphorous triamide. The reaction mixture was stirred, under reflux, for 26 h, and then the toluene was removed by distillation at atmospheric pressure. The resulting oil was distilled (bp 54–55 °C (0.1mmHg)) to yield 12.7 g (91%) of a colorless oil: ^{31}P NMR (CD_2Cl_2) δ 117.7; ^{13}C NMR (CD_2Cl_2) δ 32.5 (d, CH_3–, J_{CNP} = 23.7 Hz), 51.3 (d, –CH_2N(P)CH_2, J_{CNP} = 4.1 Hz), 55.8 (d, CH_3N(P)CH_2–, J_{CNP} = 8.5 Hz); ^{1}H NMR ($CDCl_3$) δ 2.5 (d, J_{HCNP} = 10.0 Hz, 6 H), 3.0 (m, 8 H).

Immediately before using, this material was distilled at reduced pressure, for example at 35–36 °C (0.01mmHg).

Reaction of 11 with 2,3-Butanedione (4). To a solution of 0.94 g (5.9 mmol) of freshly distilled **11** dissolved in 1 mL of methylene chloride and cooled to −78 °C was added a solution of 0.51 g (5.9 mmol) of 2,3-butanedione in 1 mL of methylene chloride. After the mixture was stirred for 2–3 min at this temperature, the solvent was removed at reduced pressure. The residual solid was immediately dissolved and stored at −78 °C: ^{31}P NMR (CD_2Cl_2) (−78 °C) δ −31.3; ^{13}C NMR (CD_2Cl_2) (−78 °C) δ 10.7 (d, CH_3C, J_{CCOP} = 10.0 Hz), 10.9 (d, CH_3C, J_{CCOP} = 11.9 Hz), 36.1 (d, CH_3N, J_{CNP} = 2.3 Hz), 43.35 (d, CH_2N(P)CH_2–, J_{CNP} = 7.6 Hz), 47.5 (d, CH_3N(P)CH_2–, J_{CNP} = 21.4 Hz), 126.5 (s), 130.35 (d, J_{COP} = 2.8 Hz).

Reaction of 11 with Benzil (12). Into 0.84 g (4.0 mmol) of **12**, cooled to −78 °C, was distilled (35–36 °C (0.01mmHg)) 0.63 g (3.95 mmol) of **11**. The resulting gummy solid was dissolved in 3 mL of methylene-d_2 chloride at −78 °C, under argon; slowly crystals formed. After three recrystallizations, under these conditions the material was sublimed (105–108 °C (0.01mmHg)) to afford 0.153 g (24.3%) of **14**: mp 145 °C; ^{31}P NMR (CD_2Cl_2) δ −30.6; ^{13}C NMR (CD_2Cl_2) δ 36.7 (d, CH_3NP, J_{CNP} = 2.1 Hz), 44.3 (d, CH_2N(P)CH_2, J_{CNP} = 8.1 Hz), 48.5 (d, CH_3N(P)CH_2, J_{CNP} = 21.9 Hz), 126.6 (s, meta), 127.0 (s, meta), 127.3 (s, para), 127.9 (s, para), 128.4 (s, ortho), 128.6 (s, ortho), 132.3 (d, J_{CCOP} = 12.2 Hz), 132.4 (d, J_{COP} = 1.8 Hz), 132.7 (d, J_{CCOP} = 9.8 Hz), 135.8 (d, J_{COP} = 3.0 Hz); ^{1}H NMR (CD_2Cl_2) δ 2.84 (d, J_{HCNP} = 9.1 Hz, 6 H), 2.63–3.42 (m, 8 H), 7.17–7.77 (m, 10 H). Anal. Calcd for $C_{20}H_{24}N_3O_2P$: C, 65.03; H, 6.55. Found: C, 65.13; H, 6.80.

Preparation of 2,6,10-Triazaundecane. A mixture of 189 g (1.0 mol) of 3,3′-iminodipropanoic acid dimethyl ester[5] and 70 g (2.3 mol) of methylamine was heated in a 500-mL stainless-steel autoclave at 100 °C for 6 h. The oil which resulted was washed with three 500-mL portions of ether to yield ca. 185 g of crude amide. Attempts to purify this material failed. The crude amide was added slowly to a stirred, under nitrogen, suspension of 76 g (2 mol) of $LiAlH_4$ in 800 mL of dry tetrahydrofuran. After the addition was completed the mixture was heated under reflux for 24 h. After the reaction mixture was cooled in an ice-water bath there was added, with good stirring, 76 mL of water, 76 mL of 15% sodium hydroxide and finally 250 mL of water. After being stirred for 1 h at room temperature the mixture was separated by filtration. The solid was washed with 3 L of tetrahydrofuran and this was combined with the filtrate. After concentration at reduced pressure there remained an oil which was distilled (bp 75–80 °C (0.07 mmHg)) to yield 86 g (54%) of product: ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 3 H, NH), 1.65 (quintet, J_{HCCH} = 7 Hz, 4 H, –$CH_2CH_2CH_2$), 2.40 (s, 6 H, –NCH_3), 2.65 (t, J_{HCCH} = 7 Hz, 4 H, CH_3NCH_2– or –N(H)CH_2, 2.68 (t, J_{HCCH} = 7 Hz, 4 H, CH_3N(H)CH_2 or –N(H)CH_2).

Preparation of 2,10-Dimethyl-2,6,10-triaza-1-phosphabicyclo[4.4.0]decane (16). To a stirred solution of 25.35 g (0.159 mol) of 2,6,10-triazaundecane in 30 mL of toluene, heated under nitrogen to 70 °C, was added 26.02 g (0.159 mol) of hexamethylphosphorous triamide. The mixture was heated at 90 °C for 24 h, and then the toluene was removed at reduced pressure. The residual oil was distilled (bp 59 °C (0.15mmHg)) to yield 25.7 g (86%) of a colorless liquid: ^{31}P NMR ($CDCl_3$) δ 116.9; ^{13}C NMR ($CDCl_3$) δ 23.6 (d, –CH_2CH_2NP, J_{CCNP} = 2.8 Hz), 39.5 (d, CH_3NP, J_{CNP} = 27.4 Hz), 48.4 (d, –CH_2N(CH_3)P or –CH_2NP, J_{CNP} = 4.0 Hz), 48.7 (d, CH_2N(CH_3)P or –CH_2NP, J_{CNP} = 5.1 Hz); ^{1}H NMR ($CDCl_3$) 0.95–2.10 (m, 4 H, –$CH_2CH_2CH_2$), 2.50 (d, J_{HCNP} = 13 Hz, 6 H, CH_3NP), 2.15–3.80 (m, 8 H, –CH_2NP′ and –CH_2N(CH_3)P).

Reaction of 16 with Benzil (12). To a stirred solution of 0.374 g (2 mmol) of **16** dissolved in 1.5 mL of methylene-d_2 chloride under a nitrogen atmosphere was added 0.42 g (2 mmol) of benzil in 2 mL of methylene-d_2 chloride. No purification was attempted: ^{31}P NMR (CD_2Cl_2) δ −37.1; ^{13}C NMR (CD_2Cl_2) (25 °C) δ 25.7 (s, –$CH_2CH_2CH_2$–), 40.2 (d, CH_3NP, J_{CNP} = 2.6 Hz), 48.7 (d, –CH_2N(CH_3)P, J_{CNP} = 5 Hz), 50.8 (d, –CH_2NP, J_{CNP} = 1.6 Hz), 126.5 (s, meta), 127.13 (s, para), 128.4 (s, ortho), 133.1 (d, ipso, J_{CCOP} = 10.6 Hz), 133.9 (s, olefinic); (−7 °C) all resonances are present and relatively sharp except for the olefinic carbons which were at coalescence; (−55 °C) δ 25.2 (s, –$CH_2CH_2CH_2$), 39.8 (d, CH_3NP, J_{CNP} = 3.0 Hz), 48.2 (d, –CH_2N(CH_3)P or –CH_2NP, J_{CNP} = 2.9 Hz), 50.3 (s, –CH_2N(CH_3)P or –CH_2NP), 125.6 (s, meta), 126.5 (s, meta′), 127.5 (s, para), 127.6 (s, para′), 128.3 (s, ortho), 131.1 (d, olefinic, J_{COP} = 3.2 Hz), 132.3 (d, ipso-equatorial, J_{CCOP} = 11.4 Hz), 132.5 (d, ipso-axial, J_{CCOP} = 9.9 Hz), 136.0 (s, olefinic′); ^{1}H NMR (CD_2Cl_2) δ 1.50–2.10 (m, 4 H, –$CH_2CH_2CH_2$), 2.85 (d, J_{HCNP} = 10 Hz, 6 H, CH_3NP), 2.15–4.0 (m, 8 H, –CH_2NP and –CH_2N(CH_3)P).

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