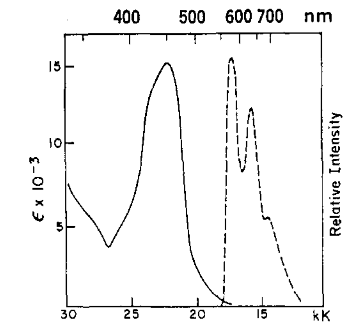

Figure 1. Room-temperature absorption spectrum (—) of aqueous $Ru(bipy)_3Cl_2$ and its corrected emission spectrum (---) at 77°K in an ethanol–methanol (4/1 v/v) glass.[15]

data in this Stern–Volmer plot establishes that the quenching is predominantly a diffusion-controlled process; static quenching would affect the intensity but not the lifetime. The Stern–Volmer quenching constant, K_{SV}, given by the slope of the plot, is $4.42 \times 10^3\ M^{-1}$. The bimolecular quenching constant, k_2, is $6.5 \times 10^9\ M^{-1}\ sec^{-1}$ ($k_2 = K_{SV}/\tau_0$, our value for τ_0 being 0.685 μsec), which is close to the diffusional encounter limit (see ref 17).

Sensitized reaction of the $PtCl_4^{2-}$ in deoxygenated $1 \times 10^{-3}\ M$ $HClO_4$ was established as follows. Irradiated (450 nm) and dark solutions, after removing the $Ru(bipy)_3^{2+}$ with a cation exchanger, were compared spectrophotometrically. The spectral differences were consistent with the principal product being $PtCl_3(H_2O)^-$; the observed isosbestic points at 340, 370, and 420 nm are close to the reported ones at ~345, 380, and 428 nm.[18]

Kinetic evidence confirmed the product assignment. The second-order rate constant for Cl^- anation of $PtCl_3(H_2O)^-$ (prepared by aging a solution of $PtCl_4^{2-}$) agreed within 5% with that measured, after removal of the donor, for a sensitized solution. From back-anation experiments, apparent aquation yields of 0.052-0.067 were obtained ($[PtCl_4^{2-}] = 1.6$–$1.7 \times 10^{-3}\ M$, $[Ru(bipy)_3^{2+}] = 1.6 \times 10^{-4}\ M$). Since the yield for disappearance of the donor (determined fluorometrically) is less than 0.01, a chemical sensitization path can essentially be ruled out.

The photochemical and quenching data give a limiting sensitized aquation yield of 0.07 ± 0.01. Reaction 3 of ref 6 may be written

$$T + C \xrightarrow{k_2} S + C^* \text{ or } C \quad (1)$$

$$C^* \xrightarrow{\phi^*} \text{products} \quad (2)$$

We conclude that ϕ^* is at least 0.07, a value substantially less than for direct photolysis of $PtCl_4^{2-}$ at 472 nm,[18] 0.17. Since the intersystem-crossing yield for $Ru(bipy)_3^{2+}$ is close to unity, possible explanations for the difference between the direct photolysis and the sensitized yields are the following: (a) process 1 may produce C^* ~40% of the time, (b) the state C^* and the one reached following 472-nm excitation may well be different and have different photochemical properties, (c) the aquation of C^* may occur during the encounter lifetime and hence in an environment chemically different from that of C^* as directly populated. Further experiments may allow some discrimination among these possibilities.

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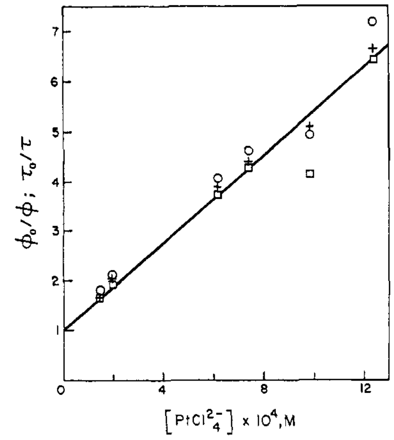

Figure 2. Quenching of the emission of $Ru(bipy)_3Cl_2$ in 1×10^{-3} M $HClO_4$ by $PtCl_4^{2-}$: +, lifetime data ($\tau_0 = 0.685$ μsec); ○ and □, relative intensity data taken before and after the lifetime measurements, respectively. $[Ru(bipy)_3^{2+}] = 3.4 \times 10^{-4}\ M$ (deoxygenated).

In conclusion, we wish to emphasize that $Ru(bipy)_3^{2+}$ and analogous compounds exhibiting CT emissions[12,19,20] have much to recommend them as low-energy sensitizers in both organic and inorganic photochemical studies. The large extinction coefficients ($\epsilon > 10^4$) allow the use of low sensitizer concentrations and facilitate the detection of donor–acceptor chemical reactions. The intrinsic luminescences allow rapid visual detection of donor quenching; systems exhibiting no quenching need not be studied for sensitization. Molecular engineering, as by modifying the metal or the ligands, makes a wide range of donor triplet-state energies available;[21] and, of course, unlike many organic sensitizers, the complexes are water soluble. Finally, the remarkable ability of $Ru(bipy)_3^{3+}$ to exhibit chemiluminescence with various reductants[22] may be valuable to those wishing to probe the relation between photophysical processes and those of thermal reaction kinetics. It is possible, for example, that the mechanism of radiationless deactivation and of thermal activation is essentially the same.

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1,6-Diphosphatriptycene

Sir:

The preparation of heterocycles containing phosphorus has been the subject of numerous papers in

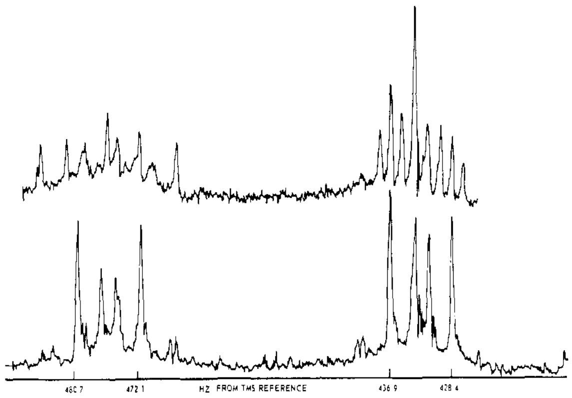
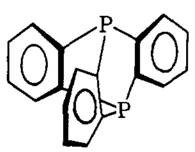
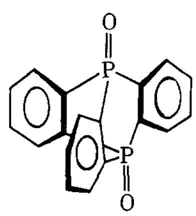


Figure 1. Top: pmr spectrum of diphosphatriptycene (ν_0(TMS) = 59,994,716 Hz). Bottom: ^{1}H spectrum with ^{31}P decoupled (ν_1 = 24,285,265 Hz).

recent years.[1] A recent publication dealing with the synthesis and physical data of azaphosphatriptycene[2] prompts us to disclose the synthesis and characterization of 1,6-diphosphatriptycene (I), a novel heterocyclic system containing two phosphorus atoms in a bridgehead position.



I



II

This substance is prepared in a one-step synthesis by treating *o*-dichlorobenzene and white phosphorus in the presence of catalytic amounts of ferric chloride. A typical reaction procedure is as follows: 68.2 g (2.2 g-atoms) of white phosphorus, 588 g (4.0 mol) of *o*-dichlorobenzene, and 8.1 g (0.05 mol) of anhydrous ferric chloride are heated in a sealed glass tube at 280° for 4 hr. The crystalline product after filtering, washing with cold methanol, and recrystallizing from tetrachloroethylene is obtained in a yield of 20% (59.4 g) as a white solid, melting at 323–325°. Other products formed in this reaction include phosphorus trichloride, *o*-chlorophenylphosphine dichloride, and di(*o*-chlorophenyl)phosphine chloride.

The results of the elemental analysis suggested that compound I had the empirical formula $C_{18}H_{12}P_2$. (*Anal.* Calcd: C, 74.46; H, 4.14; P, 21.35. Found: C, 74.12; H, 4.07; P, 21.19.) This was confirmed by the mass spectrum of I which showed a strong parent peak at 290. Prominent fragment peaks were observed at *m/e* 290, 257, 183, and 107. Doubly and triply charged parent ions were also observed.

The ultraviolet spectrum of I in 40% ethanol shows absorption bands at 218 ($\epsilon_{max} \simeq 1.03 \times 10^5$), 267 ($\epsilon_{max} = 1.86 \times 10^3$), 275 ($\epsilon_{max} = 2.16 \times 10^3$), and 283 m$\mu$ ($\epsilon_{max} = 2.28 \times 10^3$). Its infrared spectrum in KBr shows strong bands at 1431, 1258, 1230, 1160, 1105, 750, 725, 545, and 473 cm^{-1}.

(1) For a review see G. Markl, *Angew. Chem., Int. Ed. Engl.*, **4**, 1023 (1965).
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The proton magnetic resonance (pmr) spectrum, shown in Figure 1, occurs entirely in the region expected for protons attached to aromatic rings. The splitting is exceedingly complex. The molecule has 14 nuclei with spins of $^1/_2$ (twelve ^{1}H, two ^{31}P), which can give rise to 16,384 energy levels. These may be classified according to total ^{1}H spin, total ^{31}P spin, and assuming the proposed structure, molecular symmetry (D_{3h}). It is possible to simplify the problem further by assuming all coupling constants between protons in different rings to vanish. Even then the spectrum remains too complicated to analyze, since the coupling of protons in different rings to the ^{31}P nuclei renders them interdependent. It is possible, however, to remove this interpendence by spin decoupling the ^{31}P; in this case, if the assumed structure is correct and if protons in different rings are not coupled, the spectrum should reduce to independent sets of four spins grouped into two symmetrically equivalent pairs (AA′BB′ case). This pattern is easily recognized, containing up to 24 lines symmetrically distributed about a central point.

The result of a spin decoupling experiment is shown in Figure 1. A typical AA′BB′ spectrum is obtained at a single, sharp ^{31}P irradiation frequency. It is possible to analyze the ^{31}P-decoupled proton spectrum to obtain the individual H,H coupling constants.[3] In the AA′XX′ approximation, an analysis yields: $|J_{AA'}|, |J_{XX'}| = 7.4, 0.4$ Hz; $J_{AX} = \pm 7.4$ Hz; $J_{AX'} = \pm 1.2$ Hz; $\delta_A, \delta_B = 7.94, 7.21$ ppm. These are in clear agreement with a symmetrically ortho-disubstituted benzene ($J_{ortho} = 7.4$, $J_{meta} = 1.2$, $J_{para} = 0.4$ Hz).[3]

The ^{31}P chemical shift calculated from the optimum decoupling frequency[4] is 43 ppm upfield from an 85% H_3PO_4 external reference. This is intermediate between those reported for azaphosphatriptycene (80 ppm)[2] and triphenylphosphine (8 ppm),[5] reflecting a progressive distortion of the C–P–C bond angle which the caged structure would require.

By reaction of 1,6-diphosphatriptycene with an excess of benzyl bromide a quaternary monobenzylphosphonium bromide was formed which gave analytical data consistent with the monobenzyl bromide of I. (*Anal.* Calcd for $C_{25}H_{19}P_2Br$: C, 65.07; H, 4.12; P, 13.43; Br, 17.35. Found: C, 64.97; H, 4.11; P, 13.36; Br, 17.18.) The probable reason that only the monobenzyl bromide was formed is that this material was so insoluble in the reaction mixture that it did not react any further. Oxidation of I with peracetic acid in ethyl acetate gave the dioxide, II. (*Anal.* Calcd for $C_{18}H_{12}P_2O_2$: C, 67.08; H, 3.72; P, 19.25. Found: C, 67.35; H, 3.73; P, 19.18.)

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