

Table II. Calculation of Excited-State Bond Strengths^a for Cr(tacn)X₃ Compounds

X	bond strength, μm^{-1}		diff, kJ mol^{-1}	ligand loss predicted
	Cr-N	Cr-X		
F	0.898	1.46	196	nonane
Br	0.898	0.890	0.9	Br ⁻
CN	0.898	1.09	23	nonane
NCS	0.898	0.916	2.1	nonane

^a Based on the ligand field parameters for ammonia and X ligands given in ref 11.

yield, 0.05, relatively independent of solvent, in agreement with theoretical expectations that this should be the minor mode of reaction.

This complex, being thermally and relatively photostable and emitting efficiently with a long doublet lifetime, meets well the criteria of this study and will be a useful addition to the available quenching and energy-transfer species. It is noteworthy that in degassed solution the emission yield is 0.01, a value that compares very favorably with 0.002 in dmsol for *trans*-Cr(cyclam)(NH₃)₂²⁺²⁴ and that approaches the 0.034 for Ru(bpy)₂²⁺.²²

Consistent with its long lifetime, the molecule is quenched by oxygen, ferric and silver ions, and the complexes Cr(CN)₆³⁻ and Cr(en)₃³⁺. The last case is interesting in that the doublet energy of the acceptor is higher than that of the donor, 1.49²⁵ and about 1.39 μm^{-1} , respectively (the latter value is estimated from the onset of emission and is approximate). The most likely explanation of this is an uphill, thermally activated process, although other mechanisms are conceivable. The given doublet energies show that energy transfer in this direction must overcome a Boltzmann factor of 0.008 at 298 K. It is to be noted that this is not inconsistent with the ratio of the bimolecular quenching constants for the two complex ions studied, 0.03, the first of which is for conventional, exothermic energy transfer but is slower than expected for the diffusion-controlled process. Energy-transfer quenching should lead to sensitized emission, but this could not

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be observed owing to the much more efficient emission from the unquenched donor complex. We intend to pursue these aspects further in a future study.

The quenching by silver and ferric ions is unlikely to occur either by energy or electron transfer. A possible mechanism is binding to the free S end of the coordinated isothiocyanate; this would perturb the excited doublet state and may well catalyze intersystem crossing to the ground state.

The scavenging of oxygen on photolysis of aerated dmsol solutions is an interesting phenomenon. Two mechanisms might be considered: redox reaction with dmsol of the doublet excited state of the complex, arising because of its greater oxidation potential, or energy transfer to produce singlet oxygen, which then reacts with dmsol or impurities such as dimethyl sulfide. Of these two possibilities the second seems more likely, on the basis of the uniqueness to dmsol of the process and the known reactivity of singlet oxygen with dimethyl sulfide.²⁶

These results show that this molecule fulfills the criteria that we set out to meet. It is sufficiently thermally and photochemically stable to allow energy-transfer studies. It has a doublet state of long lifetime that can be quenched by a number of metal ions, complexes, and other species such as molecular oxygen. This implies in turn its potential utility as a sensitizer of low-energy excited states. Since the molecule is neutral and soluble in nonaqueous solvents, it allows the possibility of quenching and sensitization studies without the complexities associated with ionic species in nonaqueous media.

Acknowledgment. The authors wish to thank the University of Victoria and The Natural Sciences and Engineering Research Council of Canada for financial support. Dr. A. McAuley kindly provided us with an initial sample of the tacn ligand, and D. Kneeland, W. Riske, T. Ward, and P. A. Warren generously assisted with various aspects of the experiments.

Registry No. Cr(tacn)(CO)₃, 88253-23-0; Cr(tacn)Br₃, 112421-66-6; Cr(tacn)(CN)₃, 112421-67-7; Cr(tacn)(NCS)₃, 112421-68-8; Cr(tacn)F₃, 112421-69-9; Br₂, 7726-95-6; O₂, 7782-44-7; Fe³⁺, 20074-52-6; Ag⁺, 14701-21-4; Cr(CN)₆³⁻, 14875-14-0; Cr(en)₃³⁺, 15276-13-8; dmsol, 67-68-5; dmf, 68-12-2; Cr(tacn)(dmsol)₃³⁺, 112421-70-2.

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Notes

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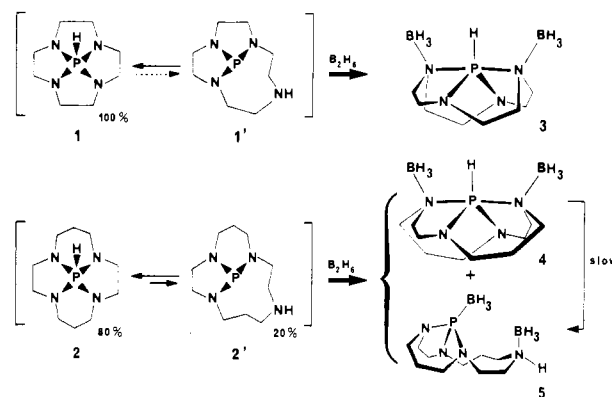
Relevance of the Acid-Base Phosphorane/Phosphorane Equilibrium to the Tautomeric Phosphorane/Phosphine Equilibrium in the Action of an Activated Ketone on Tetracyclic Tetraaminophosphoranes

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We recently reported the unexpected difference in behavior of cyclenphosphorane **1** and cyclamphosphorane **2** toward the same Lewis acid, B₂H₆¹ (Scheme I). Compound **1** was found to react readily with diborane to yield the bis adduct **3** in which no rearrangement of the initial structure has occurred whereas **2**, which is known to be in equilibrium with an open form in solution, led to a mixture of closed cyclamphosphorane-bis(borane) **4**, analogous to **3**, and an open cyclamphosphine-bis(borane) **5**.

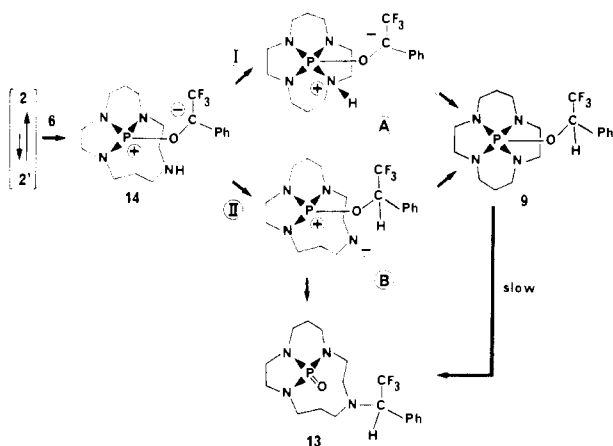
Scheme I. Reactivity of **1** and **2** toward Diborane



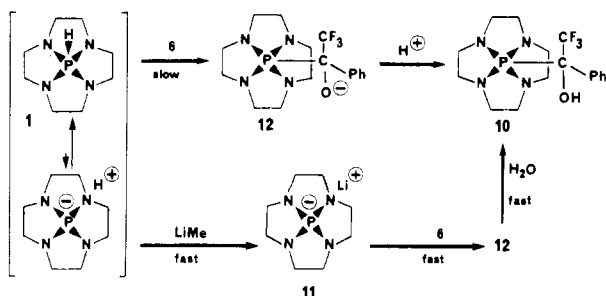
In this paper, we have investigated the reactivity of **1** and **2** toward an activated ketone, trifluoroacetophenone (**6**), in order (i) to reveal a possible open tautomeric form for **1**, (ii) to know whether **2** reacts as a phosphorane or a phosphine toward the ketone, and (iii) to evaluate the part of the NH site in the open form.

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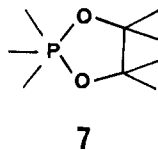
Scheme II. Reactivity of 2 toward 6



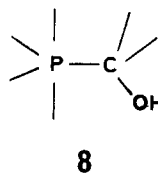
Scheme III. Reactivity of 1 toward 6



Tertiary phosphines are well known to react with two equivalents of activated ketone such as hexafluoroacetone and trifluoroacetophenone (**6**), usually leading to dioxaphospholanes such as **7**, as a result of an oxidative addition process on phosphorus.²



By contrast, P-H-containing phosphorus compounds such as hydrophosphines, phosphonates and hydrophosphoranes tend to react with only one equivalent of ketone leading, respectively, to phosphine alcohols, phosphonate alcohols and phosphorane alcohols **8**.³



We describe here the unexpected difference in reactivity of cyclenphosphorane **1** and cyclamphosphorane **2** toward the same activated ketone, with the synthesis and the characterization of the phosphorane alkoxide **9** (Scheme II) and the phosphorane alcohol **10** (Scheme III). We demonstrate the important part played in that reactivity by the phosphorane/phosphoranide acid-base equilibrium.

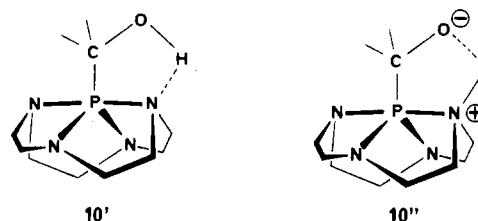
Results and Discussion

Reaction between 2 and 6. Compound **2** reacts instantaneously with **1** or **2** equiv of **6** in pentane at $-70\text{ }^\circ\text{C}$, giving the cyclamphosphorane alkoxide **9**, which is isolated in 70% yield, excluding the formation of a dioxaphospholane 1:2 adduct such as **7**.

Structure of **9** is unambiguously established by its analytical and spectroscopic data. The ^{31}P NMR spectrum of **9** in toluene exhibits a signal at -56 ppm, characteristic of 5-connected phosphorus. The presence, in the ^{19}F and ^1H NMR spectra, respectively, of a doublet at -75.9 ppm ($^3J_{\text{FH}} = 7.5$ Hz) and a doublet of quadruplets at 5.7 ppm ($^3J_{\text{HF}} = 7.5$ Hz; $^3J_{\text{HP}} = 15$ Hz) is only consistent with the P-O-CH(CF₃)Ph moiety, excluding the isomeric phosphorane alcohol structure, which could also be expected.

When **9** is left at $-30\text{ }^\circ\text{C}$ in a sealed tube in a toluene solution, it converts, slowly but totally, to its structural isomer **13**. The ^{31}P NMR spectra of **13** presents a singlet at 25.5 ppm which is a typical chemical shift for a tris(dialkylamino)phosphine oxide. The NCH(CF₃)Ph moiety is established in the ^{19}F NMR spectrum by a doublet at -78.2 ppm ($^3J_{\text{FH}} = 7.5$ Hz), which is further confirmed by a quadruplet at 5.2 ppm ($^3J_{\text{HF}} = 7.5$ Hz) in the ^1H NMR spectrum. We note that **13** is also present in the crude mixture in about 15% (based on the ^{31}P NMR).⁴

Reaction between 1 and 6. Cyclenphosphorane **1** reacts slowly with one equivalent of **6** in pentane at room temperature, yielding quantitatively compound **10**, which is remarkably stable in solid and in solution. Its formulation is supported by its analytical and spectroscopic data, which do not, however, allow a clear definite distinction between the two forms **10'** and **10''**. The ^{31}P NMR



spectrum exhibits a signal at -35 ppm, characteristic of 5-connected phosphorus, and the ^{19}F NMR spectrum shows a doublet at -71.8 ppm ($^3J_{\text{FP}} = 3$ Hz) in agreement with structure **10**. The ^{13}C NMR spectrum consists of, in addition to the expected signals for the phenyl carbons, a quadruplet for the CF₃ carbon at 126.5 ppm ($^1J_{\text{CF}} = 285$ Hz), a doublet of quadruplet for the asymmetric quaternary carbon at 79 ppm ($^1J_{\text{CP}} = 132$ Hz; $^2J_{\text{CF}} = 27$ Hz), and two doublets for the methylenes at 43.0 ppm ($^2J_{\text{CP}} = 10$ Hz) and 42.6 ppm ($^2J_{\text{CP}} = 9$ Hz). A variation of temperature does not affect the latter spectrum. The magnetic inequivalence of the methylenes is due to the asymmetric quaternary carbon, which renders them diastereotopic and anisogamic.

The ^1H NMR spectrum of **10** in CDCl₃ at room temperature presents a doublet at 8.9 ppm ($J = 20$ Hz), which disappears by addition of D₂O. This coupling constant is consistent with either $^3J_{\text{HOCP}}$ or $^2J_{\text{HNP}}$ values,^{3c,5} for **10'** or **10''**, respectively. In the infrared spectrum the two possible vibrations $\nu(\text{OH})$ and $\nu(\text{NH})$ are expected to be found in the $2500\text{--}3200\text{-}$ and $2250\text{--}2700\text{-cm}^{-1}$ regions,⁶ respectively. However, the only change observed in the spectrum after deuteration of **10** is the occurrence of a band at 2050 cm^{-1} . The relation $\nu(\text{XH}) = 1.41(\nu(\text{XD}))$ ($X = \text{O}, \text{N}$) establishes that the original band should appear at 2890 cm^{-1} . This

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- (4) Compounds **9** and **13** possess asymmetric carbon and phosphorus atoms, and each compound should therefore exist as a pair of diastereoisomers. The detection of only one type of signals is probably due to the fact that, in the case of **13**, both diastereoisomers unfortunately have indiscernible chemical shifts and, in the case of **9**, an exchange between them through a pseudorotation mechanism at phosphorus exists.
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value would be in favor of **10'** (strong O—H...N interaction) rather than **10''**.

Comparison between the Reactivities of 1 and 2. It is particularly noteworthy that the two closely related phosphoranes **1** and **2**, which differ only by the number of methylene groups, exhibit a quite different reactivity toward **6**: **2** reacts *instantaneously* with 1 equiv of **6** to yield the P—O—C sequence containing adduct **9** whereas **1** reacts *slowly* with 1 equiv of **6** to give the P—C—O sequence containing compound **10**.

This difference may be assigned to the presence, for **2**, of the open tautomeric form cyclamphosphine. It is generally assumed that the initial site of attack of tertiary phosphine on activated ketone is located on oxygen, producing a phosphonium-carbanion 1:1 intermediate, which reacts rapidly with a second ketone to give dioxaphospholane.^{2a} The observed reactivity of **2** may thus be attributed to the aminophosphine open form **2'** and would involve phosphorus, its most nucleophilic site, leading to the intermediary compound **14**. This may evolve to give **9** either (i) by intramolecular nucleophilic addition of the free nitrogen site on the phosphorus followed by transprotonation (Scheme II, route I) or (ii) by direct abstraction of the N-bound proton by the carbanion site followed by an intramolecular attack of the amide on the phosphonium site (route II).

The presence of the NH tentacle in the intermediate **14** probably inhibits the formation of a dioxaphospholane, which might have been expected if **2'** behaved as a typical tertiary phosphine. Protonation of the carbanion and ring closure are probably more rapid than condensation with a second equivalent of ketone.

It should be noted that the presence of **13** in the crude mixture in about 15% cannot arise only from the slow transformation of **9**. It may be taken to indicate that intermediate B (route II) is formed: this intermediate evolves either to **9**, by addition on the phosphonium site, or to **13** by nucleophilic attack at the POC carbon and formation of the P=O bond.

On the other hand, **1** seems to exhibit the expected P—H reactivity of phosphoranes toward **6** with the formation of the phosphorane alcohol **10**. However, it has been proposed that the hydrospiroposphoranes react by their open form,^{3c} yielding a P—C—O compound, by the attack of phosphorus on the carbonyl carbon atom. This cannot be the case for **1**: its open form **1'** is structurally and electronically very close to **2'**; therefore, we would have expected the formation of the P—O—C compound analogous to **9** through attack of phosphorus on the carbonyl oxygen atom.

Furthermore, the basicity of the apical nitrogen atoms in **1**^{a,c} and the acidity of the P—H bond in phosphoranes have also been established.⁷ These results may be taken to indicate that the conjugated base of **1**, cyclenphosphoranide anion **11**,⁸ might react with **6**, through attack at the carbon atom of the ketone, to give **12** as depicted in Scheme III. This seems to be confirmed by the fact that **11**, obtained quantitatively by deprotonation with LiMe,⁹ reacts *instantaneously* with **6** to give **10** (after hydrolysis). By this work, we have contributed to establishing that the hydrophosphorane/phosphoranide acid-base equilibrium must be taken into account in the reactivity of tetracyclic tetraamino-phosphoranes, especially when the phosphorane/phosphine tautomeric equilibrium is not operating.

Experimental Section

Compounds **1** and **2** were prepared according to Richman's method.¹⁰ **C₁₈H₂₆N₄POF₃** (**9**). A 0.183-g (1.05-mmol) sample of **6** (Aldrich) in 20 mL of hexane is added, at -70 °C, to a solution of **2** (0.249 g, 1.10 mmol) in 40 mL of hexane. The reaction mixture is immediately filtered and concentrated, and a crystallization in pentane at -30 °C yields 0.317 g (70%) of **9** as white needles. **9** is soluble in all common organic solvents

but evolves into **13** in a few weeks in CH₂Cl₂, CHCl₃, or toluene. Anal. Calcd for C₁₈H₂₆N₄POF₃ (*M*_r, 402): C, 53.73; H, 6.51; N, 13.92; P, 7.69. Found: C, 53.07; H, 6.54; N, 13.93; P, 7.69. ³¹P{¹H} NMR (toluene): δ -56 (s). ¹⁹F NMR (C₆D₆): δ -75.9 (d, ³J_{PF} = 7.5 Hz). ¹H NMR (C₆D₆): δ 7.4 (m, C₆H₅), 5.7 (dq, ³J_{HF} = 7.5 Hz, ³J_{HP} = 15 Hz, H-(CCF₃Ph)), 2.8 (m, CH₂N), 1.55 (m, CH₂(CH₂N)₂). MS (chemical ionization with NH₃; *m/e*): MH⁺ (100%).

C₁₆H₂₂N₄POF₃ (**10**). A 0.126-g (0.70-mmol) sample of **6** in 20 mL of pentane is added dropwise to a solution of **1** (0.145 g, 0.70 mmol) in 50 mL of pentane, at -70 °C. The reaction mixture is then allowed to warm to room temperature and stirred for 4 h. The solvent is evaporated, and crystallization in CH₂Cl₂ by slow evaporation yields 0.230 g (85%) of **10** as white parallelepipedic crystals. Compound **10** is very soluble in CH₂Cl₂ and CHCl₃ and quite soluble in pentane, toluene, and CH₃CN; mp 145 °C. Anal. Calcd for C₁₆H₂₂N₄OPF₃ (*M*_r, 374): C, 51.34; H, 5.92; N, 14.97; P, 8.27. Found: C, 51.24; H, 5.88; N, 15.01; P, 8.28. ³¹P{¹H} NMR (CDCl₃): δ -35 (q, ³J_{PF} = 3 Hz). ¹⁹F NMR (CDCl₃): δ -71.8 (d, ³J_{FP} = 3 Hz). ¹H NMR (CDCl₃): δ 8.9 (d, *J*_{HP} = 20 Hz, H(O or N)), 7.5 (m, C₆H₅), 2.8 (m, CH₂N). ¹³C NMR (CDCl₃): δ 138.6, 127.5, 126.9 (C₆H₅); 126.5 (q, ¹J_{CF} = 285 Hz, CF₃); 79.0 (dq, ¹J_{CP} = 135 Hz, ²J_{CF} = 27 Hz, C(CF₃(Ph)OH)); 43, 42.5 (d, d, ²J_{CP} = 10 Hz, ²J_{CP} = 9 Hz, CH₂N). MS (chemical ionization with NH₃, *m/e*): MH⁺ (46%).

Synthesis of 10 from 11. A 0.35-mL aliquot of a 1.6 N solution of CH₃Li in ether is added dropwise to 0.102 g (0.51 mmol) of **1** in 10 mL of THF at -45 °C to give **11** (³¹P NMR (THF): δ 4.5). A 0.100-g (0.57-mmol) sample of **6** in 5 mL of THF is added to the reaction mixture at -45 °C to give **12**, which is immediately hydrolyzed by about 0.5 mL of H₂O. The solvent is pumped away, and the crude mixture is washed with 3 × 10 mL of toluene. The toluene is evaporated to yield 0.165 g of **10** (87%).

Registry No. **1**, 64317-97-1; **2**, 64317-99-3; **6**, 434-45-7; **9**, 112460-78-3; **10**, 112460-80-7; **11**, 112460-81-8; **13**, 112460-79-4.

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Emission Properties of Tetrahedral M(dppp)₂ Complexes (M = Pd, Pt). Crystal and Molecular Structure of Pt(dppp)₂

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Reports on the electronic spectroscopy and photochemistry of d¹⁰ ML₃ and d¹⁰-d¹⁰ M₂L₆ (L = P-donor) complexes have recently appeared.^{1,2} Absorptions attributable to p ← d transitions have been identified, and the lowest emissive excited states have been assigned (³[(d_{xy}, d_{x²-y²)]³(p_z)¹], ML₃; [³(dσ*)¹(pσ)¹], M₂L₆).² Most of these complexes possess long-lived excited states that are capable of undergoing photooxidative substitution with elimination of a phosphine ligand. In particular, the mononuclear and binuclear palladium complexes photoreact readily with halogenated hydrocarbons and aromatic compounds to produce oxidized species in which two electrons per metal atom have been transferred.¹}

Little is known about the effects of structural perturbations on the excited-state lifetimes and energies of d¹⁰ species. For this reason, we have measured the lifetimes and electronic spectra of M(dppp)₂ (M = Pd, Pt; dppp = bis(diphenylphosphino)propane) complexes in the solid state and in fluid solutions at room temperature and at 77 K, and comparisons of these properties to those of trigonal-planar (d¹⁰ ML₃) species have been made. In connection with this work, the structure of Pt(dppp)₂ has been determined by X-ray crystallography.

Experimental Section

Materials. K₂PtCl₄ and K₂PdCl₄ (Aldrich) and triphenylphosphine and dppp (Strem) were used without further purification. M(PPh₃)₃ and M(dppp)₂⁴ (M = Pd, Pt) were prepared according to standard proce-

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 (9) The reaction is selective. A variation of temperature or concentration does not affect the ³¹P NMR spectrum.
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