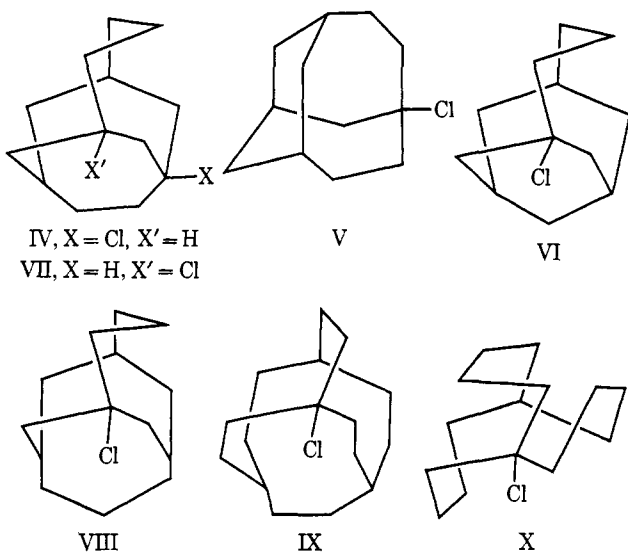


Table II. Predicted Rate Constants for Reactive Bridgehead Systems

Compounds	Bingham force field ^a		Engler force field ^b	
	$\Delta H(\text{calcd}),^c$ kcal/mol	$k(\text{calcd}),^d \text{ sec}^{-1}$ 70°, 80% EtOH	$\Delta H(\text{calcd}),^e$ kcal/mol	$k(\text{calcd}), \text{ sec}^{-1} \text{ }^f$ 70°, 80% EtOH
1-Tricyclo[5.4.1.1 ^{3,9}]tridecyl chloride (IV)	-3.75	2.6×10^{-1}	-3.64	4.5×10^{-2}
6-Tricyclo[4.4.1.1 ^{3,9}]dodecyl chloride (V) ^g	-3.87	2.8×10^{-1}	-4.73	1.5×10^{-1}
3-Tricyclo[5.3.1.1 ^{3,9}]dodecyl chloride (VI) ^h	-4.35	4.2×10^{-1}	-6.13	3.7×10^{-1}
1-Bicyclo[3.3.3]undecyl chloride (I, X = Cl)	-6.77	2.9	-8.36	2.5
3-Tricyclo[5.4.1.1 ^{3,9}]tridecyl chloride (VII)	-7.35	4.7	-8.32	2.5
1-Tricyclo[5.5.1.1 ^{3,9}]tetradecyl chloride (VIII)	-8.05	8.3	-10.43	15.
1-Tricyclo[5.5.2.2 ^{4,10}]tetradecyl chloride (IX) ⁱ			-17.38	5.4×10^3
1-Bicyclo[4.4.4]tetradecyl chloride (X)	-14.94	2.0×10^3	-20.80	1.2×10^3

^a See ref 3. ^b See ref 7. ^c Difference of strain energy between carbenium ion and corresponding hydrocarbon. ^d Calculated from eq 2. ^e Difference of steric energy between carbenium ion and corresponding hydrocarbon. ^f Calculated from $-\log k(\text{chlorides}, 80\% \text{ EtOH}, 70^\circ) = (0.37)\Delta H + 2.70$, based on the treatment given in ref 6. ^g 1,3-Bishomoadamant-6-yl chloride. ^h 1,1-Bishomoadamant-3-yl chloride. ⁱ Hexahomoadamant-1-yl chloride.



hedral value¹² and an sp² hybridized carbon is more readily accommodated at the bridgehead. Flattening at the bridgehead also reduces the repulsive nonbonded interactions involving the C-3, C-7, and C-10 methylene groups. A similar, but smaller, solvolytic rate enhancement is exhibited by monocyclic cyclooctyl derivatives.¹³ Since the three faces of I-Cl consist of chair-boat cyclooctane rings, the rate enhancement observed for I-Cl can be considered to be another manifestation of the "middle ring effect."¹³

The success of our calculations in predicting bridgehead reactivities^{3,7} has led us to search for other reactive bridgehead systems by computation. All of the polycyclic systems listed in Table II are predicted by both force field treatments^{3,7} to be significantly more reactive than *tert*-butyl chloride. It has been observed recently¹⁴ that both 1,1-bishomoadamantane (VI-H) and 1,3-bishomoadamantane (V-H), like manxane (I-H), are not stable in air and form hydroperoxides. 1-Chlorobicyclo[4.4.4]tetradecane (X), expected to be even more reactive than I-Cl, would appear to be an excellent objective for experimental investigation.

(12) Engler's force field⁶ gives the following bond angles for manxane: $\angle C_2C_3C_8$, 115.2°; $\angle C_1C_2C_3$, 118.8°; $\angle C_2C_3C_4$, 118.2°. Similar values have been found experimentally for 1-azamanxane.^{4e}

(13) See A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 95; J. Sicher, *Progr. Stereochem.*, **3**, 202 (1962); H. C. Brown and K. Ichikawa, *Tetrahedron*, **1**, 221 (1957).

(14) Professor T. Sasaki, private communication.

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Sign Changes in the ¹⁵N-³¹P Directly Bonded Coupling Constant

Sir:

The measurement of directly bonded nmr coupling constants is an important experimental activity in regard to the development of bonding theory.¹ Relative sign data pertaining to the group V and group VI nuclei are particularly significant because it is here that sign changes may occur.^{1,2} Both theoretical and experimental considerations^{1,2} indicate that the couplings involving the ³¹P nucleus are predominantly dependent³ upon the phosphorus coordination number, hence it seemed important to determine the signs and magnitudes of the ¹⁵N-³¹P coupling constants in the pentacoordinate compound F₃P(¹⁵NH₂)₂, **1**,⁴ and the tricoordinate-tetracoordinate molecule, F₃P=¹⁵NP'-F₂', **2**,⁴ and to compare them with that in the tricoordi-

(1) (a) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964); (b) W. McFarlane, *Quart. Rev., Chem. Soc.*, **23**, 187 (1969); (c) C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, **51**, 2790 (1969).

(2) C. J. Jameson, *J. Amer. Chem. Soc.*, **91**, 6232 (1969).

(3) Other factors can be important in, e.g., heterocyclic phosphines. See, e.g., D. Gagnaire, J. B. Robert, and J. Verrier, *Chem. Commun.*, 819 (1967); G. A. Gray and S. E. Cremer, *J. Chem. Soc., Chem. Commun.*, 451 (1974).

(4) These compounds were synthesized by replacing ammonia with 96.5% ¹⁵N enriched ammonia in the literature preparations. For **1** see M. Lustig and H. W. Roesky, *Inorg. Chem.*, **9**, 1289 (1970); for **2** see G. E. Graves, D. W. McKennon, and M. Lustig, *ibid.*, **10**, 2083 (1971).

nate phosphine $(\text{CF}_3)_2\text{P}^{15}\text{NH}_2$, **3**.⁵ The nmr data for **1** are consistent with a trigonal bipyramidal structure in which the NH_2 groups occupy equatorial positions.⁶ The relative sign data which are presented in Table I

Table I. The Signs and Magnitudes for Some Nmr Coupling Constants of **1**, **2**, and **3**

Coupling	J , Hz	$K(10^{20} \text{ cm}^{-3})^a$	Types of double resonance experiments ^b
$\text{F}_3\text{P}^{15}\text{NH}_2$, 1			
$^{15}\text{N}-^{31}\text{P}$	-81.54	+165.34	} $^1\text{H}-[^{31}\text{P}]$, $^{31}\text{P}-[^1\text{H}]$, $^{19}\text{F}-[^1\text{H}]$, $^{19}\text{F}-[^{19}\text{F}]$
$^{31}\text{P}-^{19}\text{F}_a^c$	-672.08	-146.79	
$^{31}\text{P}-^{19}\text{F}_e^c$	-791.58	-172.89	
$^{31}\text{P}-\text{N}-^1\text{H}$	+14.51	+2.98	
$^1\text{H}-\text{N}-\text{P}-^{19}\text{F}_a^c$	+20.71	+1.83	
$^1\text{H}-\text{N}-\text{P}-^{19}\text{F}_e^c$	-1.81	-0.16	
$\text{F}_3\text{P} = ^{15}\text{NP}'\text{F}'_2$, 2 ^d			
$^{15}\text{N}-^{31}\text{P}$	-53.20	+107.5	} $^{31}\text{P}-[^{31}\text{P}]$
$^{15}\text{N}-^{31}\text{P}'$	+93.76	-189.6	
$(\text{CF}_3)_2\text{P}^{15}\text{NH}_2$, 3			
$^{15}\text{N}-^{31}\text{P}$	+52.60	-106.66	} See ref 5
$^{31}\text{P}-\text{N}-^1\text{H}$	-14.21	-2.92	

^a For definition of K see ref 11. ^b See ref 7, 8, and 9. ^c F_a = axial fluorine, F_e = equatorial fluorine in a trigonal bipyramidal structure. ^d See ref 12.

were obtained by a combination of spin tickling,⁷ nuclear Overhauser effect,⁸ and selective decoupling⁹ experiments. All the signs for **1** have been related to a negative sign for the directly bonded $^{31}\text{P}-^{19}\text{F}$ coupling¹⁰ can therefore be considered absolute.

One noteworthy feature of the data (Table I) is the finding that the sign of the directly bonded coupling, $K_{^{15}\text{N}-^{31}\text{P}}$,¹¹ is negative in **3** and positive in **1**. Furthermore, homonuclear $^{31}\text{P}-[^{31}\text{P}]$ double resonance experiments on **2** demonstrate that the signs of the two directly bonded $^{15}\text{N}-^{31}\text{P}$ couplings are different¹² in the same molecule. Negative to positive sign changes have also been observed in the directly bonded $^{13}\text{C}-^{31}\text{P}$ ¹³ and $^{31}\text{P}-^{31}\text{P}$ ¹⁴ couplings when the coordination number of phosphorus is increased from 3 to 4 or 5.

(5) A. H. Cowley, J. R. Schweiger, and S. L. Manatt, *Chem. Commun.* 1491 (1970).

(6) Dynamic nmr studies have established that at 25° (on the nmr time scale): (i) axial-equatorial fluorine positional interchange is slow and (ii) rotation around the N-P bonds is rapid. The four amino protons are therefore coupled equally to the axial or equatorial fluorine ligands at 25°. See E. L. Muettterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 5674 (1972).

(7) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962).

(8) K. Kuhlmann and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **85**, 1010 (1963).

(9) R. Freeman, K. A. McLauchlan, J. I. Musher, and K. G. R. Pachler, *Mol. Phys.*, **5**, 321 (1962).

(10) The $^{31}\text{P}-^{19}\text{F}$ coupling constant has been shown to be absolute negative, see D. L. VanderHart, H. S. Gutowsky, and T. C. Farrar, *J. Chem. Phys.*, **50**, 1058 (1969).

(11) Since the ^{15}N nucleus possesses a negative magnetogyric ratio, comparisons between coupling constants are best made by employing the reduced coupling constant, K_{AB} , which is defined by the equation $K_{AB} = (2\pi/\hbar\gamma_A\gamma_B)J_{AB}$ where γ_A and γ_B are the magnetogyric ratios of nuclei A and B, respectively.

(12) The homonuclear ^{31}P double resonance experiments (Table I) do not yield the absolute signs of the two $^{15}\text{N}-^{31}\text{P}$ coupling constants. However, by analogy with **1** and **3** $K_{^{15}\text{N}-^{31}\text{P}}$ (tetra-coordinate) and $K_{^{15}\text{N}-^{31}\text{P}'}$ (tricoordinate) are expected to be positive and negative, respectively.

(13) (a) W. McFarlane, *Chem. Commun.*, 58 (1967); (b) W. McFarlane, *Proc. Roy. Soc., Ser. A*, **306**, 185 (1968); (c) H. Dreeskamp, C. Schumann, and R. Schmutzler, *Chem. Commun.*, 671 (1970); (d) R.-M. Lequan, M.-J. Pouet, and M.-P. Simonin, *J. Chem. Soc., Chem. Commun.*, 475 (1974).

(14) C. W. Schultz and R. W. Rudolph, *J. Amer. Chem. Soc.*, **93**, 1898 (1971), and references therein.

Qualitatively the sign changes in $K_{^{15}\text{N}-^{31}\text{P}}$ seem to relate to the changes in hybridization at the phosphorus atom. In **3** and the tricoordinate phosphorus atom of **2** the bonding description is essentially $(3p)^3$ ($\sim 0\%$ P(3s) character) while in the tetra-coordinate phosphorus atom of **2** and the equatorial plane of trigonal bipyramidal **1** the bonding schemes are sp^3 (25% P(3s) character) and the $3s3p^2$ (33.3% P(3s) character), respectively. Note that as $K_{^{15}\text{N}-^{31}\text{P}}$ changes from negative to positive then becomes progressively larger as the percent of P(3s) character increases. This correlation is understandable in terms of the model of Jameson and Gutowsky^{1c} in which increasing the valence s character (e.g., at phosphorus) causes a changeover in the dominant coupling mechanism from an indirect negative (core polarization) interaction to a direct positive (Fermi contact) interaction.

The difference in sign in the $^{31}\text{P}-\text{N}-^1\text{H}$ coupling in **1** and **3** is also of interest. The sign of, e.g., the $^{31}\text{P}-\text{C}-^1\text{H}$ coupling is also dependent on the phosphorus coordination number; however K_{PCH} changes from positive to negative when the phosphorus coordination number is increased.¹⁵ The sign difference in the equatorial and axial $^{19}\text{F}-\text{P}-\text{N}-^1\text{H}$ couplings is also noteworthy since in the analogous phosphorane, $(\text{CH}_3)_2\text{PF}_3$, both F-P-C-H couplings are positive;^{13c} however, it is significant that the equatorial coupling is appreciably smaller than the axial coupling.

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Excimeres of a Transition Metal Complex

Sir:

Excimer and exciplex formation is a widespread phenomenon for aromatic molecules.¹⁻³ In the field of transition metal complexes the formation of excimers or exciplexes has been invoked only in a few cases⁴⁻⁶ and, to our knowledge, excimer or exciplex

(1) C. A. Parker, "Photoluminescence of Solutions," Elsevier, Amsterdam, 1968.

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(4) D. G. Whitten, I. G. Lopp, and P. D. Wildes, *J. Amer. Chem. Soc.*, **90**, 7196 (1968).

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(6) G. Sergeeva, A. Chibisov, L. Levshin, and A. Karyakin, *J. Chem. Soc., Chem. Commun.*, 159 (1974).