Figure 2. Molecular orbital diagram for $CH_3\overline{NCH_2CH_2N(CH_3)}P$-$Mo(\eta^5\text{-}C_5H_5)(CO)_2$. The outside columns represent the orbital eigenvalues of the ligand fragments and metal. The center column represents the orbital energies of the complex.

atom in **2**, which is in part responsible for the large downfield ^{31}P NMR shift.[11] The combined results of the structural and theoretical studies of **1** show that the novel ligation properties of phosphenium ions warrant additional intensive study.

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(15) The spectroscopic properties of **1** prepared here are identical with those reported in our earlier work.[11] The ^{13}C NMR parameters have been redetermined: δ 87.66, 51.87 (J_{CNP} = 3.7 Hz), 33.85 (J_{CNP} = 16.1 Hz).
(16) X-ray intensity data were collected at 298 K by the θ–2θ technique with Mo $K\alpha$ radiation on a Syntex P3/F automated diffractometer equipped with a graphite-crystal monochromator, scintillation counter, and pulse height analyzer. Of a total of 3102 independent reflections examined with $3° \leq 2\theta \leq 55°$, 2219 (72%) had $I \geq 2\sigma(I)$, and these were used in the structure determination and refinement. The structure was solved by Patterson methods and refined by anisotropic least-squares techniques[17] to yield $R_1(F)$ = 4.9% and $R_2(F)$ = 6.2% at the present stage of refinement.
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(29) The calculations for **1** also reveal synergic interactions which lead to a net -0.096 charge on each CO ligand and a net -0.072 charge on the Cp ring.

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Hydroxyphosphorane Intermediates in Substitution Reactions at Phosphorus in Acyclic Phosphonofluoridates: Evidence from Nuclear Magnetic Resonance

Sir:

It is widely accepted that trigonal bipyramidal (TBP) hydroxyphosphoranes (such as **3**) or their conjugate bases, phosphoranoxide anions (such as **2**), are intermediates in nucleophilic displacements at tetracoordinate phosphorus in cyclic P=O bond containing compounds.[1] Thermally[2] and hydrolytically[3] stable cyclic hydroxyphosphoranes and phosphoranoxide anions have recently been prepared. Spectroscopic evidence for equilibrium between a cyclic hydroxyphosphate[4] or hydroxyphosphinate[3] and five-membered-ring hydroxyphosphoranes in solution has been reported. However, with acyclic phosphorus substrates[5] it has been more difficult to find compelling evidence for existence of such conformationally mobile pentacoordinate species as intermediates in substitution at phosphorus. It has been suggested that the stability of such intermediates is determined by the relative apicophilicity[6] of the nucleophile[7] and the leaving group,[8] in addition to the structural features known[3] to stabilize hypervalent species.

Scheme I
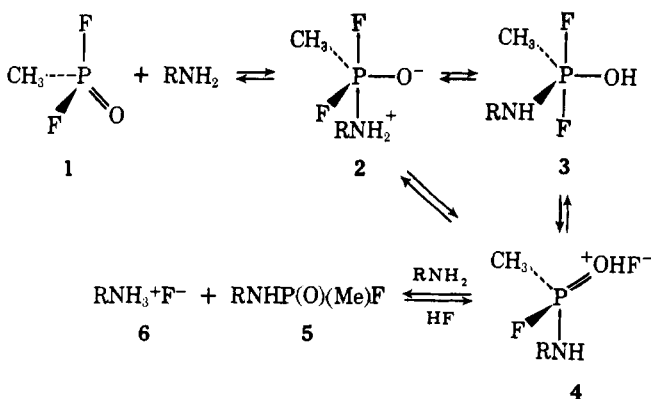
Tertiary or secondary amines and methylphosphonic difluoride (1) have been reported[9] to give a "labile complex". This "labile complex" is characterized by a doublet for the CH_3P resonance in the ^1H NMR spectra, compared with the typical doublet of triplets (dt) exhibited by 1. However, "the ability of primary amines to collapse the ^1H NMR signals of 1 could not be studied, since amide formation was quite rapid under the experimental conditions".[9] Conversely, diisopropyl phosphorofluoridate has been found[10] to be unreactive toward n-butylamine. These observations suggested to us that judicious choice of the acyclic phosphorus substrate, nucleophile, and experimental conditions may allow the long desired observation of a TBP phosphorane intermediate.

We now report evidence from NMR spectroscopy, consistent with phosphorane intermediates in the reactions of 1 with aniline or n-butylamine. The same intermediate is detected in the reaction of amide 5 (R = n-butyl) with hydrogen fluoride.

We find that treatment of 1 with Et_3N in C_6D_6, $CDCl_3$, or without solvent gives the results previously reported.[9] However, in CCl_4 1 retains the doublet of triplets (1.92 ppm, $^2J_{HP}$ = 19 Hz, $^3J_{HF}$ = 6 Hz) in the ^1H NMR spectrum after addition of Et_3N. This profound solvent effect suggests an equilibrium involving 1 and amines with polar species. More importantly, 1 (0.1 g, 1 mmol) and aniline (93 mg, 1 mmol) in $CDCl_3$ (0.4 mL) at ambient temperature show a doublet (1.70 ppm, $^2J_{HP}$ = 19 Hz) for the CH_3P resonance, typical of the "labile complex" mentioned earlier. Under these conditions amide formation could not be detected after 5 days. Moreover, refluxing 1 and aniline (2 equiv) in CCl_4 for 4 h gives no detectable 5 (R = Ph). Upon increasing the aniline concentration and the temperature, amide 5 (R = Ph) is gradually formed.[11] Anilide 5 (R = Ph) is characterized by the typical doublet of doublets of its $CH_3P(O)F$ resonance in its ^1H NMR spectrum.[11] In contrast to the instantaneous change of the dt to a doublet in the ^1H NMR spectrum of 1 upon addition of aniline (or n-butylamine), formation of 5 is surprisingly slow, contradicting the earlier reports.[9] This observation alone [5b] might be explained by slow development of a steady-state concentration of a pentacoordinate intermediate from 1.

We propose that the rapid equilibrium and fluorine exchange shown in Scheme I lead to the observed ^1H NMR phenomenon described above. This appears to be the first NMR evidence which supports a phosphorane intermediate in a displacement reaction at phosphorus in an acyclic phosphorus compound.

It should be noted that 4 (protonated 5) can be obtained directly from 2 by P–F bond cleavage. The pK_a of hydroxyphosphorane 3 may be low enough[2b,3a] to allow a large concentration of phosphoranoxide zwitterion 2 relative to that of acid 3. Isomerization of TBP species by ionization, such as in Scheme I, involving tetrahedral species has also been considered for some stable phosphoranes[12] and pentacoordinate metal

hydrides[13] and is strongly favored for several stable sulfuranes.[14]

Scheme I is also consistent with the ^{31}P NMR observed for a solution of 1 in aniline, which shows a broad triplet (line width $\nu_{1/2}$ = 140 ± 10 Hz) with chemical shift value very close to that of pure 1 (28.0 ppm). Upon decreasing the temperature, the broad triplet sharpens gradually and at −40 °C becomes a triplet of quartets ($^1J_{PF}$ = 1115 Hz, $^3J_{PH}$ = 19 Hz). A fluorine exchange process as a part of an equilibrium lying close to 1 accounts for the ^1H and ^{31}P NMR spectra.

It has been reported[15] that several phosphorus amides react with anhydrous HF to give fluoridates. These reactions probably proceed through intermediates such as 2–4. Therefore, we have reasoned that the validity of Scheme I could be tested by reacting 5 with HF. Indeed, addition of 5 (R = n-butyl) to a solution of HF in $CDCl_3$ (in a polyethylene vial) leads to an exothermic reaction. The ^1H and ^{31}P NMR spectra obtained for this solution were superimposable on those of an equimolar mixture of 1 and n-butylamine, thus substantiating Scheme I.[16]

These observations provide experimental evidence compatible with the phosphorane centered mechanism[1] of substitution at tetracoordinate phosphorus. In fact, Scheme I represents this associative pathway coupled with deprotonation of 4 after apical departure of fluoride. The quaternary ammonium group, as in phosphoranoxide zwitterion 2, is known[10,17] to be a good leaving group. Consequently, departure of this group is successfully competing with that of fluoride, thus enabling observation of the equilibrium shown in Scheme I. Further stabilization of intermediates 2 or 3 is rendered by the relatively strong P–F bond[10] which generally contributes to the stability of fluorophosphoranes.[18]

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(11) Amide 5 (R = Ph) is conveniently prepared by heating an equimolar mixture of 1 and aniline at 120–160 °C for 2 days: mp 148 °C; ^1H NMR (Me_2SO-d_6) δ 1.33 (3 H, dd, $^2J_{HP}$ = 18, $^3J_{HF}$ = 6 Hz, Me), 6.20 (1 H, br s, NH), 6.70–7.27 (5 H, m, H–Ar); ^{31}P NMR (Me_2SO) δ +22.2 (dq, $^1J_{PF}$ = 970, $^2J_{HP}$ = 18 Hz). Amide 5 (R = n-butyl) is prepared by stirring 2 equiv of n-$BuNH_2$ with 1 in benzene for 18 h, filtration, and distillation: bp 123–125 °C (0.2 mmHg); ^1H NMR δ 0.95 (3 H, m, MeC), 1.45 (4 H, m, CH_2), 1.61 (3 H, dd, $^2J_{HP}$ = 17, $^3J_{HF}$ = 6 Hz, MeP), 2.95 (2 H, m, CH_2N), 4.16 (1 H, m, HN); ^{31}P NMR δ +37.7 (d, $^1J_{PF}$ = 1010 Hz).
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(16) An additional line of evidence can be cited favoring the postulate of a small amount of phosphorane being present as a reaction intermediate. The ^{31}P and ^{19}F NMR spectra of the crude reaction mixture of 1 and excess aniline showed the presence of two (isomeric?) compounds: δP −115.1 and −131.9 (upfield from 85% H_3PO_4) (triplets of quartets, $^1J_{PF}$ = 836, $^2J_{PH}$ = 19 Hz); δF 29.9 and 30.3 downfield from CF_3CO_2H (doublets of quartets, $^1J_{FP}$ = 840, $^3J_{FH}$ = 6 Hz). These data suggest that the byproducts are hexacoordinate phosphoride zwitterions which contain the CH_3PF_2 structural unit. We tentatively suggest 7 as a likely structure for these compounds which have not been isolated yet. This observation may provide further support for the phosphorane intermediates postulated above, assuming that 7 may be formed from 2 (or 3) and aniline.

PhNH₂⁺ 群 structure

7
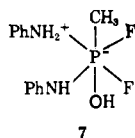
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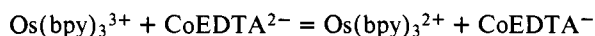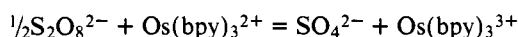## Stereoselectivity in Electron-Transfer Reactions

Sir:

Previous attempts to observe stereoselectivity in outer-sphere redox reactions have failed. Such asymmetric induction, that is, a rate difference for the reaction of enantiomers with a given chiral compound, has been searched for both by rate studies with separate enantiomers[1] and in competition experiments where racemic mixtures react with a chiral complex.[1,2] In the latter case, searches for deviation from pseudo-first-order kinetics, as one enantiomer preferentially reacts first, and for optical rotation in the final product mixture have been made. These results seem to suggest that, at least in some cases of outer-sphere electron transfer, the reactants are not in contact in the transition state.

In several of these studies, an important factor seems to have been overlooked: that of racemization of any chiral product by electron exchange with its reduced form. For example, $Cr(phen)_3^{2+}$, used as a reductant in several of the experiments, racemizes at 0.123 s^{-1}.[3] The self-exchange rate for $Cr(phen)_3^{3+/2+}$ is not known, but it is undoubtedly close to that of $Cr(bpy)_3^{3+/2+}$ for which 10^7 M^{-1} s^{-1} has been estimated.[4] Thus, even at $Cr(phen)_3^{2+}$ concentrations as small as $\sim 10^{-7}$ M, $Cr(phen)_3^{3+}$ will be kept racemic owing to oxidation by it of racemic $Cr(phen)_3^{2+}$. Asymmetric induction experiments are usually carried out with the net rate of oxidation less than the racemization rate of the reductant. Thus the reductant always presents a racemic mixture, and optically active product may be racemized as quickly as it is formed.

We have investigated some systems that do not suffer from this limitation and have discovered what we believe to be the first cases of stereoselectivity in outer-sphere electron transfer. We will first report results for systems, where, by taking into account the properties of the reactants, we are certain that the reactions are of the outer-sphere type.

In the reaction to be dealt with first, to avoid having to use high concentrations of the chiral oxidant, the reaction was carried out catalytically. The net change involved $S_2O_8^{2-}$ oxidizing $CoEDTA^{2-}$ to $CoEDTA^-$, with $Os(bpy)_3^{3+/2+}$ as the catalyst, according to the sequence

$$\frac{1}{2}S_2O_8^{2-} + Os(bpy)_3^{2+} = SO_4^{2-} + Os(bpy)_3^{3+}$$

$$Os(bpy)_3^{3+} + CoEDTA^{2-} = Os(bpy)_3^{2+} + CoEDTA^-$$

Each of these stages is known from independent observations to proceed readily.

A sample of 3.7×10^{-6} M 59% optically pure $[\Delta(-)_{546}Os(bpy)_3](ClO_4)_2$[5,6] was dissolved in a aqueous solution of 8×10^{-4} M $Na_2CoEDTA\cdot2HClO_4$ with 0.03 N sodium persulfate as oxidant, pH 2.1. Within an hour formation of $CoEDTA^-$ was complete. After cation exchange to isolate the $CoEDTA^-$, CD and optical rotation measurements indicated an optical excess of $2.9 \pm 0.3\%$ $\Delta(+)_{546}CoEDTA^-$[7] or

5.0 ± 0.5% after accounting for the purity of the Os reactant. A sample of the $[\Lambda(+)_{546}Os(bpy)_3](ClO_4)_2$ reacts to produce the $\Lambda(-)_{546}CoEDTA^-$ in the same yield.

In a similar experiment with optically pure $[\Lambda(+)_DRu(bpy)_3](ClO_4)_2$,[8] the product proved to be 0.4 ± 0.2% $(+)_{546}CoEDTA^-$. Preliminary results indicate that $\Delta(-)_DCo(bpy)_3^{3+}$,[9] $\Delta(+)Fe(phen)_3^{3+}$,[10] and $\Lambda(-)Fe(bpy)_3^{3+}$[11] react stereoselectively with $CoEDTA^{2-}$ to give several percent optically pure (+)-, (−)-, and $(+)_{546}CoEDTA^-$, respectively, but the results with this group of oxidants are difficult to quantify owing to racemization of the oxidant. It should be noted that no general trend emerges, since, in the cases of $Os(bpy)_3$ and $Co(bpy)_3$, the Δ forms lead to preference for $\Delta(+)_{546}CoEDTA^-$, while it is the Λ forms of $Ru(bpy)_3$, $Fe(bpy)_3$, and $Fe(phen)_3$ that do so. Also, the amounts of induction are all rather small. The 5.0% induction for $Os(bpy)_3^{3+}$ means that the rate ratio is only 52.5/47.5 or 1.11 between the Δ and Λ forms of reductant, corresponding to a difference in activation free energy of ~ 50 cal/mol.

In addition to these results, we have also noted stereoselectivity in the reaction of $K[(+)_{546}CoEDTA]$[12] with excess $Co(en)_3^{2+}$, but here, because of the lability of Co(II)en complex, we cannot be as certain as in the systems already described, that the reaction is of the outer-sphere type. When 4.7×10^{-4} M $K[(+)_{546}CoEDTA]$ is added to a deaerated solution of 8.2×10^{-3} M $Co(ClO_4)_2$ in 9.6×10^{-2} M ethylenediamine, and the solution acidified after reaction, stoichiometric production of $Co(en)_3^{3+}$ is observed. CD and optical rotation analyses of the product solution indicate an optical purity of $10 \pm 2\%$ $\Delta(+)_DCo(en)_3^{3+}$.[13]

A significant enhancement of the extent of discrimination is observed in a nonprotic solvent. When 2.4×10^{-3} M $K[(+)_{546}CoEDTA]$ reacts with 0.2 M ethylenediamine and 5.2×10^{-3} M $Co(ClO_4)\cdot6H_2O$ in Me$_2$SO, an optical excess of $(1.1 \pm 0.2) \times 10^{-3}$ M $(+)_DCo(en)_3^{3+}$ is observed, or 46 ± 8% with respect to the added oxidant. These results correspond to relative rates of reaction of the Δ:Λ of $Co(en)_3^{2+}$ with ΔCoEDTA$^-$ of ~ 1.2 in the aqueous system and 2.7 in Me$_2$SO. Particularly for the reaction in Me$_2$SO, it is difficult to understand the extent of chiral discrimination if several solvent molecules are interposed between the reactants in the activated complex.

Proof that the reaction of $CoEDTA^-$ with $Co(en)_3^{2+}$ proceeds by an outer-sphere path is of critical importance, since asymmetric induction in electron transfer implies that the reactants are in intimate contact, a foregone conclusion for some inner-sphere, but not outer-sphere, electron-transfer reactions.

Rate studies at 30.0 °C, $\mu = 0.14$, have shown that the reaction of $CoEDTA^-$ with $Co(en)_3^{2+}$ follows second-order kinetics with a rate constant of 17 ± 2 M^{-1} s^{-1} ([en] = 0.56 M). Stopped-flow studies show that $Co(en)_3^{3+}$ is produced as fast as $CoEDTA^-$ disappears, within 100 ms of the start of the reaction, and we have been unable to detect an intermediate. As a result, we can estimate that any intermediate must be decomposing at >0.8 s^{-1} at 30 °C.

If the reaction were proceeding by an inner-sphere mechanism, the intermediate would be a $Co^{III}(en)_3$-$EDTACo^{II}$ species, with the Co^{III} bound to five nitrogens and one oxygen. This species would have to decompose to $Co(en)_3^{3+}$ at >0.8 s^{-1}. By way of analogy, $Co(NH_3)_5OAc^{2+}$ in ethylenediamine was found to decompose with a half-life of ~ 30 min to what appeared to be $[Co(NH_3)_5en]^{3+}$.

It is interesting to note that the results just described can account for the curious "substitution" of ethylenediamine onto $CoEDTA^-$. Dwyer et al.[14] observed that adding KCoEDTA to 50% en at 30 °C yields $Co(en)_3^{3+}$ in several minutes with "partial retention of configuration." Busch et al.[15] studied the reaction further, noting that, from $(+)_{546}CoEDTA^-$, 13.2%