water with that of the structurally similar $4(H^+)_2$·Rh(I)[14] in acetone suggests little or no rate supression due to water.[15] Catalyst $4(H^+)_2$·Rh(I) is less active than Wilkinson's catalyst by approximately a factor of 5-10 in acetone solution.

Water-soluble diphosphine-rhodium complexes show catalytic activity in potentially useful types of reactions other than homogeneous hydrogenation. For example, 4·Rh(CO)Cl[16] in the presence of fourfold excess of **4** catalyzes the shift reaction (eq 1; TN = 32 h^{-1}),[17] while 3·Rh(I)NBD$^+$Tf$^-$ in the presence of 1 equiv of added **3** catalyzes exchange between water and dihydrogen (eq 2, TN = 8 h^{-1} (0.1 M NaOAc); TN = 10 h^{-1} (0.1 M HOAc)). A similar catalysis of eq 2 was found using 7·Rh(I) in the presence of a twofold excess of **7** (TN = 5 h^{-1}).

$$CO + H_2O \xrightarrow[\text{pH 13.8, 85 °C, } P(CO) = 58 \text{ psi}]{4 \cdot Rh(I)} H_2 + CO_2 \quad (1)$$

$$H_2 + D_2O \xrightarrow[3,\ 25\ °C]{3 \cdot Rh(I)} HDO + (HD + D_2) \quad (2)$$

These results establish a practical strategy for the synthesis of water-soluble chelating diphosphine complexes of transition metals, and illustrate that the catalytic activity of these complexes in water need not be intrinsically small, nor their stability inherently low. Using these catalysts, it may be possible to effect types of transformations which cannot be easily accomplished using conventional catalysts: the homogeneous reduction of biological substrates by dihydrogen represented by FMN → $FMNH_2$ represents one such example. We will describe further applications of water-soluble phosphine-metal complexes in catalysis in subsequent publications.

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(13) The use of a phosphate buffer is not essential. The buffer employed here served only to increase the initial solubility of the substrate.
(14) $4(H^+)_2$·Rh(I) is the rhodium complex derived from **4** having both carboxylate groups protonated.
(15) 3·Rh(I) is itself insoluble in acetone; an indirect comparison is required.
(16) Preparation from $(Ph_3P)_2Rh(CO)Cl$ by exchange of **4** for Ph_3P in H_2O (pH 9.1).
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Intramolecular Ion Solvation Effects on Gas-Phase Acidities and Basicities. A New Stereochemical Probe in Mass Spectrometry

Sir:

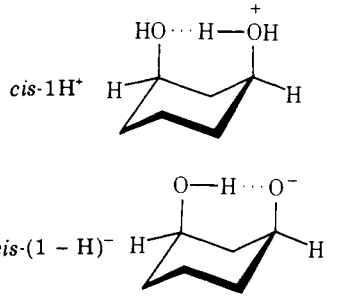
Mass spectrometric differentiation of stereoisomeric cyclic diols and related compounds based on the fragmentation behavior in chemical ionization (CI) spectra is well known.[1-5] These spectra, however, imply a second stereochemical approach.

The proton transfer processes in positive and negative CI (P CI, N CI) spectra[6-8] are outlined below (eq 1 and 2) for substrate molecules, M, and reactant Bronsted acids, AH^+, and bases, B^-. These reaction sequences depend on the proton affinities (PA) of the species involved. More exothermic proton transfer conditions are in favor of spectra with abundant parent ions, MH^+ or $(M - H)^-$ ions, and fragment ions, whereas near-thermoneutral or endothermic energetics give spectra with prominent peaks for proton bound attachment ions, MAH^+ and MB^-.

$$M + AH^+ \rightleftharpoons M\cdots H^+\cdots A \rightleftharpoons MH^+ + A \quad (1)$$

$$M + B^- \rightleftharpoons (M - H)^-\cdots H^+\cdots B^- \rightleftharpoons (M - H)^- + HB \quad (2)$$

For cyclic diols, in the first type of spectra, stereochemical control of the fragmentations is observed. The *cis*-MH^+ alkoxonium ions and *cis*-$(M - H)^-$ alkoxide ions are stabilized by intramolecular hydrogen bridging, as depicted for 1,3-cyclohexanediol (**1**) ion species; the trans isomers are generally incapable of internal H bonding and, thus, give abundant



fragment ions.[2,3,5] In the second type of spectra the MH^+/MAH^+ and $(M - H)^-$/MB^- ion intensity ratios according to reactions 1 and 2 are diagnostic terms. Field[9] has reported structural effects on MH^+/$MC_4H_9^+$ ion intensity ratios for monoalcohols, in the first instance. In CI(NH_3) spectra selective protonation of conjugated ketones has been observed.[10] Furthermore, it has been shown that the gas-phase PA of diamines can be about 80 kJ/mol higher than normal due to internal H bonds.[11] In CI spectra of open-chain diols and related compounds, intramolecular H bonding apparently leads to a similar PA shift, which causes a higher MH^+/MNH_4^+ ratio than for the monofunctional species.[12] Evidence has been presented for H-bridging effects on the MH^+/

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Table I. Partial $t\text{-}C_4H_9^+$ and NH_4^+ PCI Spectra[16] of Cyclic Diols[a-d]

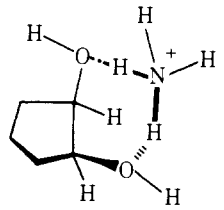
	p	$MC_4H_9^+$	MH^+	p	MNH_4^+	MH^+
cis-**1**	26		68	3	29	51
trans-**1**	23	3	13	4	54	2.2
cis-**2**	22		75	10	15	64
trans-**2**	22	3	19	4	19	0.5
cis-**3**	10	2	54	3	53	0.4
trans-**3**	14	15	10	2	56	0.4

[a] Intensities in percentage of substrate ions, $\%\Sigma_{80}$. [b] The p values are the percentage of substrate ions relative to total ionization, used as a sample pressure indication. [c] Temperature for $t\text{-}C_4H_9^+$ 100 °C (**1**, **2**) and 70 °C (**3**), for NH_4^+ 200 °C. [d] $t\text{-}C_4H_9^+$ data from ref 2.

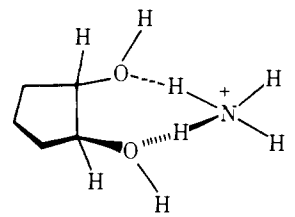
MH_3O^+ ratio of the ortho but not the other isomers of suitable difunctional phenols.[13] In line with these observations on internal H bonds, Hunt[14] has pointed out the potential of the NH_4^+ ion as a stereochemical probe of organic compounds. We now show that this stereochemical approach is valid on a wide basis. In this paper we report on PA-related stereochemical control of proton transfer in $MC_4H_9^+$, MNH_4^+, MF^-, and MCl^- adducts from 1,3- and 1,4-cyclohexanediols (**1** and **2**) and 1,2-cyclopentanediols (**3**).[15,16]

The first data on this topic (Table I) are taken from an earlier isobutane CI study.[2] As cyclic alcohols (cf. R_2CHOH with $R > C_3H_7$, PA = 825 kJ/mol)[17] are more basic than isobutene (PA = 810 kJ/mol),[8] proton transfer by $t\text{-}C_4H_9^+$ reactant ions is exothermic and, thus, abundant MH^+ ions are formed. Nevertheless, the spectra of *trans*-**1** and *trans*-**2** do show small but distinct $MC_4H_9^+$ peaks similar to secondary monoalcohols,[9] whereas *cis*-$MC_4H_9^+$ ions are practically absent. This stereochemical effect clearly reflects the increased PA of the cis diols due to internal ion solvation (see *cis*-$\mathbf{1}H^+$). The size of the effect is enhanced under less energetic conditions. For *cis*- and *trans*-**3**, the $MH^+/MC_4H_9^+$ ratio is actually reversed at very low ion source temperature (70 °C).

The PA of ammonia (841 kJ/mol)[8] lies between the cis and trans diol PA values which can be estimated from the data above. Therefore, NH_4^+ PCI, approximately thermoneutral, should be especially sensitive to diol basicity variations.[14] Accordingly, the *trans*-MH^+ peaks for **1** and **2** (Table I) are less than 3% Σ_{80}, whereas the *cis*-MH^+ ions yield about 60% Σ_{80}, in line with the increased alcohol basicity. However, the isomeric 1,2-diols **3** drastically discriminate between NH_4^+ reactant ions with strong chelating capabilities and $t\text{-}C_4H_9^+$ ions which are unable to form additional H bonds. Both epimers of **3** can attach and stabilize NH_4^+ ions within a pentagonal chelate ring with linear H bonds (see *cis*- and *trans*-



cis-$3NH_4^+$



trans-$3NH_4^+$

$3NH_4^+$). No appreciable *cis*-$3H^+$ peak is found as intramolecular diol solvation is inhibited through the chelate structure.[18]

In the negative ion attachment/detachment sequence (2), the energetic equivalent of the NH_4^+ cation above is the F^- anion (PA = 1548 kJ/mol; *cf.* $(CH_3)_2HCO^-$, PA = 1565 kJ/mol).[7] A similar inversion of the $(M - H)^-/MF^-$ intensity ratio for the configurational isomers of **1**–**3** (Table II) discloses here the intramolecular anion solvation in the cis diols (see *cis*-$(\mathbf{1} - H)^-$).[15] The identification of diol stereoisomers is also

Table II. Partial F^- and Cl^- NCI Spectra[16] of Cyclic Diols[a-c]

	p	MF^-	$(M - H)^-$	p	MCl^-	$(M - H)^-$
cis-**1**	41	10	90	0.9	95	4.6
trans-**1**	29	39	36	0.6	99	1.1
cis-**2**	48	8	92	1.0	88	12
trans-**2**	40	45	44	1.2	98	1.7
cis-**3**	30	12	88	0.3	95	4.7
trans-**3**	30	42	39	0.4	99	1.1

[a,b] See Table I. [c] Temperature 200 °C.

possible with a much weaker base than alkoxide anions. Cl^- reactant ions[19] (PA = 1393 kJ/mol)[7] generally produce high-intensity MCl^- attachment ions and small $(M - H)^-$ peaks (Table II). The cis/trans intensity ratio of $(M - H)^-$ is in favor of cis by a factor of 4–7 and again underlines the internal anion solvation.[18]

The results show that intramolecular ion solvation effects on gas-phase acidities and basicities enable the mass spectral detection of internal H bonds in cyclic diols, similar to infrared and proton magnetic resonance spectra, and, thus, the assignment of configurational isomers. It seems likely that the CI attachment ion correlations reported here[20] can be advantageously extended to stereochemical analysis of more complex molecules, including various functional groups.

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Surprising Synthesis and Reactivity of an Acidic Hydroxyphosphorane

Sir:

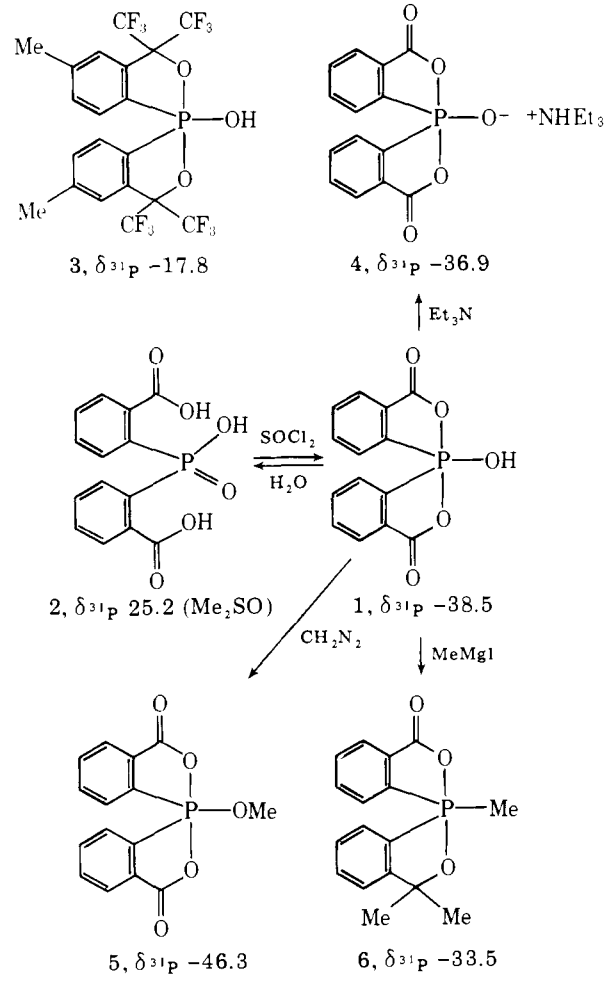
Pentacoordinate hydroxyphosphoranes, such as **1**, are usually suggested as intermediates or transition states in nucleophilic substitution at tetracoordinate phosphorus compounds possessing P=O bonds,[1] such as **2**. While a variety of isolable oxyphosphoranes are well known,[2] only very recently have we isolated the first stable hydroxyphosphorane.[3] The chemistry of this new class of pentacoordinate phosphorus hydroxy acids is practically unknown. Acidities of hydroxyphosphoranes have been estimated in the pK_a range of 10-11, 5-6,[3c] or even as "strong acids".[4] We now report a surprising synthesis of the thermally stable and acidic hydroxyphosphorane **1**,[3a] and some of its unexpected reactions.

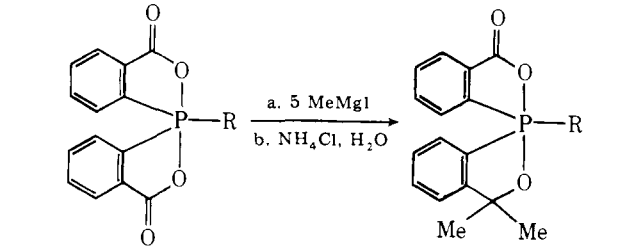
Trifluoroacetic acid (TFA) induced cyclodehydration of **2** yields a stable crystalline 1:1 complex of **1** with TFA.[3a] We now find that pure **1**, mp 266-269 °C, is obtained upon mixing **2** and thionyl chloride or bromide followed by evaporation of excess of the reagent. Moreover, **1** does not react with $SOCl_2$ or $SOBr_2$ even after 2 h at 60 °C to give a halophosphorane. This lack of reactivity, noted[3c] also for **3**, is very surprising. The acidity of **1** could not be directly determined, because it is decomposed by water. Also, the sodium phosphoranoxide produced from **1** and sodium hydride in tetrahydrofuran (THF) is practically insoluble in common organic solvents, thus preventing protonation experiments.[3c] However, the following observations suggest that **1** is more acidic than **3**, for which a $pK_a = 5.3 \pm 0.2$ has been estimated.[3c]

The chemical shift value for the CH_2 protons of Et_3N (δ 2.45 ppm) is shifted to 3.15 in $Et_3NH^+Cl^-$. The smaller chemical shift change to δ 2.77 ppm for the crystalline complex obtained from **3** and Et_3N indeed suggests that **3** is a weaker acid than acetic acid ($pK_a = 4.75$, δ_{CH_2} for Et_3NH^+ ^-OAc 2.97). Salt **4**, obtained from **1** and Et_3N,[5] shows δ_{CH_2} 3.09 indicating that **1** is a stronger acid than **3**, or even acetic acid. This is further supported by the observation that **4** does not react with methyl iodide, while the latter and the complex from **3** and Et_3N give methyltriethylammonium iodide and **3**.[3c]

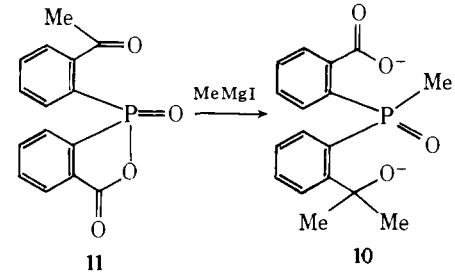
Methoxyphosphorane **5** was prepared from **1** and diazomethane[6] and characterized spectroscopically, but it could not be completely purified because of its facile hydrolysis by traces of water. In spite of the instant hydrolysis of **1** by water to give **2** (Scheme I), it does not react with dry methanol or ethanol even at reflux. More intriguing is the reaction of **1** with a sixfold excess of methylmagnesium iodide. Phosphorane **6** is obtained after refluxing the reagents for 5 h in benzene-THF (4:1), cooling, and quenching with aqueous ammonium chloride. Phosphorane **6** is also prepared from **7** and a fivefold excess of MeMgI. Phosphoranes **7** and **8** were prepared in procedures analogous to that described earlier.[3a] A crystalline precipitate was observed in the Grignard reactions of **1** and **7**, but it was too insoluble to allow recording of its ^{31}P NMR spectrum. However, the analogous reaction mixture from phosphorane **8** and MeMgI exhibited a low-field $\delta_{^{31}P}$ 57.8 prior to, and a high-field $\delta_{^{31}P}$ −19.7 after, the aqueous NH_4Cl quenching. This observation is consistent with intermediates such as **10**, which upon protonation would spontaneously be cyclodehydrated to the product phosphoranes **6** and **9**. Similar facile conversions of phosphine oxide to phosphoranes have recently been observed.[8] The surprising C-P bond formation

Scheme I





7, R = Me, $\delta_{^{31}P}$ −51.0
8, R = 2-Bu, $\delta_{^{31}P}$ −44.8, −45.0
6, R = Me
9, R = 2-Bu, $\delta_{^{31}P}$ −19.7



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