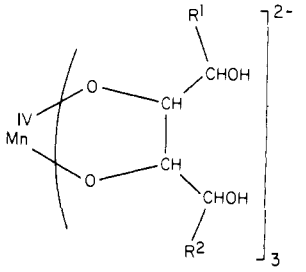

$R^1 = R^2 = CH_2OH$ (sorbitol)

$R^1 = CH_2OH$, $R^2 = CO_2H$ (D-gluconate)

$R^1 = R^2 = CO_2H$ (D-glucorate)

$R^1 = R^2 = H$ (erythritol)

Figure 2. Probable coordination geometry for tris(polyhydroxy) complexes of manganese(IV).

six-line hyperfine patterns clearly are indicative of manganese(IV) rather than manganese(II) (Figures 1d and 1e).

Addition of excess hydrogen peroxide also eliminates the EPR signal in methanol or dimethyl sulfoxide solution, and results in the evolution of dioxygen and a reduction to manganese(III) (eq 2).

The concentration of $S = 3/2$ EPR absorbing species has been estimated for the complex in dimethyl sulfoxide by use of the double integration method[27-30] (1 mM copper(II) in aqueous 10 mM EDTA was used as the integration standard). The concentration of manganese(IV) ($S = 3/2$) is ~85 ± 10% of the total manganese present.

The data are consistent with the formulation of the complex as $(Me_4N)_2Mn(C_6H_{12}O_6)_3$, a monomeric high-spin complex of manganese(IV) that exhibits an axial distortion from octahedral symmetry. This is in accord with an earlier CD study of similar complexes.[1] The large value for D, (1.3 ± 0.3) cm^{-1}, the parameter that indicates the magnitude of the axially symmetric crystalline field, is similar to that shown by several chromium(III) tris(chelates)[25] and may also be assigned to the presence of a large dipole moment in the manganese–sorbitol bonds (Figure 2). The spectra of Figure 1 are in marked contrast to the single isotropic line centered around $g = 2$ that is observed for powdered $K_2Mn^{IV}Cl_6$ at 77 K, which is known[12] to have pure octahedral symmetry. The sorbitol is believed to chelate by its *cis*-alkoxo groups, as shown in Figure 2.

This manganese(IV) complex appears to act as a specific oxygenation (oxidation) catalyst in alkali–oxygen wood pulping.[31] Preliminary results indicate that it is capable of catalyzing both ring degradation and oxidative coupling processes in alkaline solutions of several lignin model substrates.

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$$Mn^{II}(ClO_4)_2 + 3C_6H_{14}O_6 + 4Me_4NOH \underset{MeOH}{\overset{O_2}{\rightleftharpoons}} [(Me_4N)_2Mn^{IV}(C_6H_{12}O_6)_3] + 2\,Me_4NClO_4\downarrow + H_2O_2 + 24H_2O$$

The equilibrium was driven in favor of manganese(IV) by decomposition of the hydrogen peroxide with manganese dioxide.

$$2H_2O_2 \xrightarrow[MnO_2/MeOH]{} 2H_2O + O_2$$

The isolated complex contained >95% manganese(IV) on the basis of polarographic analysis and by titration with ferrous ion in aqeous 0.5 M NaOH and 0.5 M sorbitol.[1,17] An alternative method of preparation involved permanganate oxidation of manganous(II) perchlorate.

$$2KMnO_4 + 3Mn^{II}(ClO_4)_2 + 15C_6H_{14}O_6 + 14Me_4NOH \xrightarrow[aqueous\ MeOH]{} 5[(Me_4N)_2Mn^{IV}(C_6H_{12}O_6)_3] + 2KClO_4\downarrow + 4Me_4NClO_4\downarrow + 24H_2O$$

In each case the complex was isolated as a hygroscopic red-brown powder after filtration of the reaction solution and recrystallization from methanol–ethyl acetate (1:5) and was dried (0.01 Torr) for 6–8 h (yield 93%). Microanal. Calcd for $(Me_4N)_2Mn(C_6H_{12}O_6)_3 \cdot 6H_2O$: C, 36.66; H, 8.46; N, 3.29; Mn, 6.46. Found: C, 35.90; H, 8.23; N, 3.07; Mn, 6.50. The isolated complex exhibited a room-temperature bulk magnetic moment of 4.0 ± 0.1 μ_B, in agreement with that for a high spin d^3 center (μ_{eff} 3.89 μ_B).
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Water-Soluble Complexes of Tertiary Phosphines and Rhodium(I) as Homogeneous Catalysts[1]

Sir:

The low solubility of common phosphine–transition metal complexes in water has inhibited their application to catalytic transformations in aqueous solutions. Recent experiments have established that complexes derived from $Ph_2P(m\text{-}C_6H_4SO_3Na)$[2] are catalytically active in homogeneous olefin hydrogenation and hydroformylation reactions in water.[3-5] Complexes derived from bidentate ligands can have useful differences in chemical stability and catalytic activity from analogous complexes containing only monodentate ligands.[6] Here we report the development of coupling reactions which permit the facile conversion of (bis(2-diphenylphosphinoethyl)amine (**1**)[7,8] to a wide variety of water-soluble diphosphines

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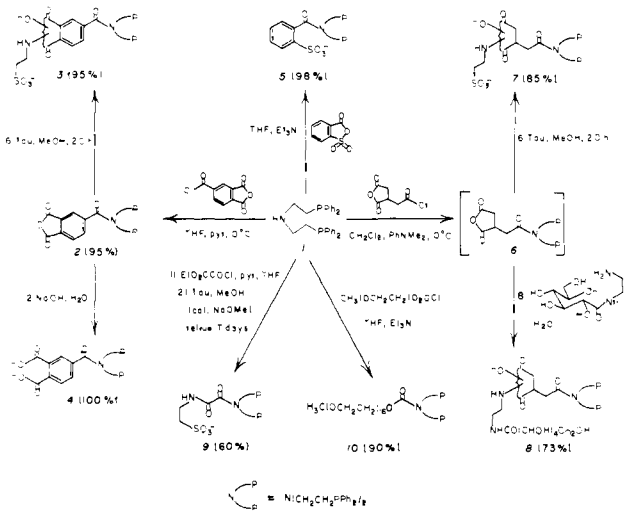
Table I. Homogeneous Hydrogenation Reactions in Water (TN = Turnover Number, h^{-1})[a]

substrate	product[b]	catalyst	TN initial, h^{-1}[c]	TN total[d]
$CH_2{=}C(NHAc)CO_2H$		**3**·Rh(I)	>200	4070 (20)[e]
(*Z*)-$PhCH{=}C(NHAc)CO_2H$			>30	600 (20)[e]
$CH_2{=}CHCONH_2$			>12	1000 (86)[e]
(*E*)-$CH_3CH{=}CHCO_2H$			13	560 (110)
(*E*)-4$(OH)C_6H_4CH{=}CHCO_2H$			13	540 (88)
(*E*)-$HO_2CCH{=}CHCO_2H$			48	970 (20)
			144[f]	259 (18)
			130[g]	570 (4.5)
$[CH_2{=}CHCH_2NCOCHOH]_2$			6.2	300 (66)
$CH_2{=}CHCH_2NHCONH_2$	$(CH_3CH{=}CHNHCONH_2)$		7.0	410 (90)
$CH{=}CH(CH_2)_3CH_2$			1.6	32 (20)
FMN[h]	$FMNH_2$[h]		5.0	300 (70)
CH_3COCO_2H	$CH_3CHOHCO_2H$		14	600 (85)[e]
$CH_2{=}CHCH_2OH$	(CH_3CH_2CHO)		19	330 (18)
		5·Rh(I)	4.4	84 (19)
		8·Rh(I)	2.0	40 (20)
		10·Rh(I)	1.5	27 (18)
		11·Rh(I)[i]	23	140 (6)
		$(PhP)_3RhCl$[j]	130	800 (6)
		4$(H^+)_2$·Rh(I)[j]	25	445 (18)
oxidized lipoic acid		**3**·Rh(I)	no reaction	
$(HOCH_2CH_2S)_2$			no reaction	
$CH_2{=}CHCH_2NHCSNH_2$			no reaction	
bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic acid			no reaction	
iron(III)			no reaction	

[a] Unless otherwise indicated, hydrogenations were carried out in 0.1 M phosphate buffer, pH 7.0, T = 25 °C, $P(H_2)$ = 32 psi. [b] The product is that derived by reduction of the C=C group unless indicated otherwise. Products derived from isomerization of the olefinic linkage are indicated in parentheses. [c] The initial turnover number ((moles of substrate transformed) (mol of Rh)$^{-1}$ h^{-1}) was calculated from data obtained over the first 20 h of reaction. [d] The total turnover is the number of moles of substrate transformed per mole of Rh in the indicated time. [e] These values represent minimum rates; the samples used were completely hydrogenated in the interval indicated. [f] T = 60 °C, $P(H_2)$ = 32 psi. [g] T = 25 °C, $P(H_2)$ = 120 psi. [h] FMN = flavin mononucleotide; $FMNH_2$ = dihydroflavin mononucleotide. [i] **11**·Rh is $[CH_3O(CH_2CH_2O)_{\sim 15}{-}CH_2CH_2PPh_2]_2Rh$. This ligand was prepared by treating $CH_3O(CH_2CH_2O)_{\sim 16}{-}H$ with thionyl chloride, followed by reaction of the resulting chloride with potassium diphenylphosphine; cf. D. Feitler, Ph.D. Thesis, MIT, 1977. [j] In acetone solution.

Scheme I. Synthesis of Water-Soluble Diphosphines (Tau = Sodium Taurinate, $NH_2CH_2CH_2SO_3^-Na^+$)[10]



(Scheme I), and a survey of the catalytic activity of rhodium complexes of several of these new ligands.

Trimellitic anhydride acid chloride, *o*-sulfobenzoic anhydride, and ethyl oxalyl chloride are commercially available; tricarballylic α,β-anhydride acid chloride was prepared by standard procedures.[9] The conditions used for the coupling reactions were unexceptional. Although the product diphosphines were difficult to purify to homogeneity, ^1H and ^{31}P NMR spectroscopy, IR spectroscopy, and solubility provided good evidence for the assigned structures. The corresponding rhodium complexes X·Rh(I)NBD^+Tf^- (NBD = norbornadiene, Tf^- = triflate) were prepared in situ and used without characterization.[10,11] Both the phosphines and the derived rhodium complexes appeared to form homogeneous solutions in water, although certain of these solutions may contain micelles, especially at high concentrations. Complex **7** appeared to be the most soluble, with a concentration in saturated aqueous solution of ~0.3 M (pH 7.0, 25 °C).

A representative hydrogenation was conducted as follows. Into a 5-mL round-bottomed flask equipped with a Teflon-coated stirring bar was weighed 3.6 mg (8.0 μmol) of $[Rh(NBD)Cl]_2$ and 4.0 mg (16 μmol) of AgTf. The flask was capped with a rubber septum and flushed thoroughly with argon. Dioxane (0.5 mL, distilled from $NaBH_4$ under argon) was added by syringe. The mixture was stirred for 5 min and the resulting yellow-orange solution decanted from the AgCl precipitate by cannula into a solution of 13.8 mg (17.5 μmol) of **3** in 1.0 mL of aqueous dioxane (1:1). The solution was stirred for an additional 15 min and transferred by cannula into an argon-flushed pressure reaction bottle (Lab Glass) containing 8.40 g (65.1 mmol) of α-acetamidoacrylic acid suspended in 200 mL of 0.1 M aqueous phosphate buffer (initial pH 7.60 before the addition of the substrate).[13] The system was purged with hydrogen for 5 min, the hydrogen pressure adjusted to 32 psi, and the reaction mixture stirred at ambient temperature. Aliquots removed from the reaction bottle by cannula under a positive hydrogen pressure were analyzed by a combination of GLC and NMR spectroscopy.

Table I summarizes the activity of these complexes in the hydrogenation of representative substrates: Most data were obtained using **3**·Rh(I)NBD^+Tf^-, since it was easy to prepare and manipulate. The order of reactivity of olefinic substrate in hydrogenation is similar to that observed in organic solvents. The catalysts are poisoned by sulfur-containing compounds. Comparison of the activity toward allyl alcohol of **3**·Rh(I) in

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}).

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

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

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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(12) The amine used in making **8** was prepared by reaction of D-glucono-δ-lactone with tenfold excess of ethylenediamine for 20 h at ambient temperature.
(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:

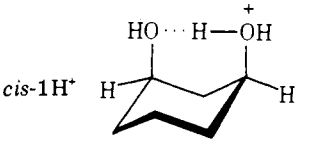
Mass spectrometric differentiation of stereoisomeric cyclic diols and related compounds based on the fragmentation behavior in chemical ionization (CI) spectra is well known.[1-5] These spectra, however, imply a second stereochemical approach.

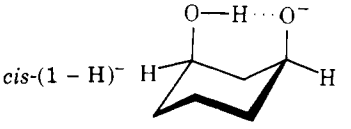
The proton transfer processes in positive and negative CI (P CI, N CI) spectra[6-8] are outlined below (eq 1 and 2) for substrate molecules, M, and reactant Bronsted acids, AH^+, and bases, B^-. These reaction sequences depend on the proton affinities (PA) of the species involved. More exothermic proton 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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