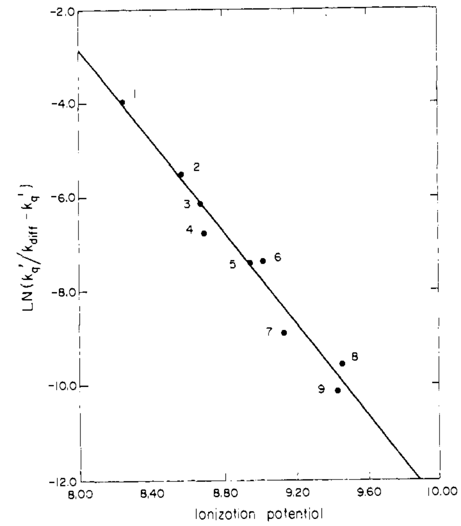


Figure 2. Fluorescence quenching of 2,3-diazabicyclo[2.2.2]oct-2-ene: (1) cyclohexadiene (IP = 8.25 eV,[11b] 8.40 eV[11a]), (2) cyclopentadiene (IP = 8.57 eV[11a]), (3) 1,3-pentadiene (IP = 8.68 eV[11a]), (4) quadricyclene (IP = 8.70 eV[11a]), (5) cyclohexene (IP = 8.945 eV[11a,b]), (6) cyclopentene (IP = 9.02 eV,[11b] 9.01 eV[11a]), (7) 2-butene (IP = 9.13 eV[11a]), (8) 1-hexene (IP = 9.45 eV[11a]), (9) 1-octene (IP = 9.43 eV[11b]). The least-squares procedure gives the empirical equation $\ln [k_q'/(k_{diff} - k_q')] = 36.4 - 4.91\text{IP}$, with k_{diff}(isooctane) = 13.9×10^9 l. mol^{-1} sec^{-1}, with a correlation coefficient of 0.9840.

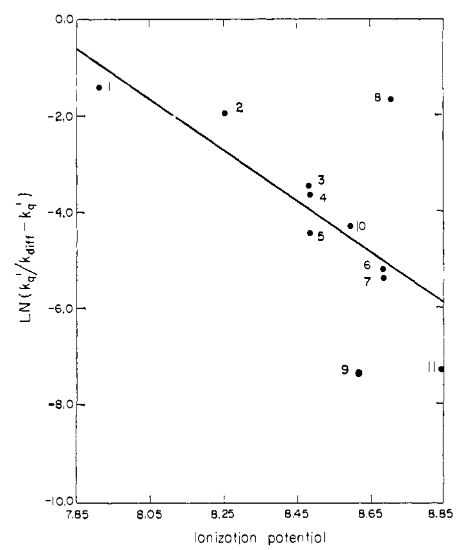


Figure 3. Fluorescence quenching of naphthalene: (1) 2,5-dimethyl-2,4-hexadiene (IP = 7.91 eV[11c]), (2) 1,3-cyclohexadiene (IP = 8.25,[11b] 8.40 eV[11a]), (3) *trans,trans*-2,4-hexadiene (IP = 8.48 eV[11c]), (4) *cis,trans*-2,4-hexadiene (IP = 8.48 eV[11c]), (5) *cis,cis*-2,4-hexadiene (IP = 8.48 eV[11c]), (6) *trans*-1,3-pentadiene (IP = 8.68 eV[11a]), (7) *cis*-1,3-pentadiene (IP = 8.68 eV[11a]), (8) quadricyclene (IP = 8.70 eV[11a]), (9) norbornadiene (IP = 8.60 eV) [this is an average of reported values 8.45,[11b] 8.62,[11d] 8.69,[11e] and 8.60 and 8.67 eV[11a]], (10) cyclopentadiene (IP = 8.57 eV[11a]), (11) isoprene (IP = 8.845 eV[11a]). The least-squares procedure gives the empirical equation $\ln [k_q'/(k_{diff} - k_q')] = 47.93 - 6.13\text{IP}$, excluding the points for quadricyclene and norbornadiene; k_{diff} (n-hexane) = 2.01 $\times 10^{10}$ l. mol^{-1} sec^{-1}. The correlation coefficient, excluding quadricyclene and norbornadiene, is 0.939.

that, to the first approximation, the assumptions of constant solvation terms and constant k_{-q} are valid.

92, 19 (1970); (f) P. Bishof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).

The data from the publications of Solomon, Thomas, and Steel[6] and Solomon, Steel, and Weller[5] on DBO fluorescence quenching are shown in Figure 2. Of the quenchers examined (the limiting factor is the availability of the ionization potentials), there is no clear evidence of any effects other than charge transfer operating on the quenching of DBO singlet state.

A linear relationship between $\ln [k_q'/(k_{diff} - k_q')]$ and ionization potential is also observed for the quenching of naphthalene fluorescence with several hydrocarbons, Figure 3. The linear relationship does not hold for some of the quenchers, notably quadricyclene and norbornadiene.[12] This anomalous behavior of quadricyclene is interesting because Solomon, Steel, and Weller[5] have concluded that the quadricyclene interaction with aromatic hydrocarbon singlet states is charge transfer in character. We believe that all of the hydrocarbons are quenching by a charge-transfer mechanism, but other effects also seem to be operating.

Thus we conclude that the above kinetic method is useful for examination of photochemical reactions and that in spite of its simplifications it can be used to detect gross reaction mechanisms. Furthermore, we conclude that the major mechanism for fluorescence quenching of naphthalene and the bicyclic azo compounds is charge-transfer interaction.

(12) Neither 2,3-dimethyl-2-butene (ΔIP $\cong$ 8.40 eV) nor 1,3-cyclooctadiene quenches the fluorescence of naphthalene[13] and so these also fall into the class of compounds which do not obey the linear relationship. Quadricyclene shows "normal" behavior in the quenching of DBO fluorescence.

(13) L. M. Stephenson, Ph.D. Thesis, California Institute of Technology, 1968, p 17.

Ted R. Evans
Research Laboratories, Eastman Kodak Company
Rochester, New York 14650
Received January 6, 1971

Rhodium Complexes with the Molecular Unit P_4 as a Ligand

Sir:

Complexes in which a stable elementary molecule is bonded to a transition metal are quite rare. Only two types have been described in the literature: O_2 complexes, for example $IrCl(O_2)CO[(P(C_6H_5)_3]_2$,[1] and N_2 complexes, for example $IrCl(N_2)[P(C_6H_5)_3]_2$.[2] An interesting candidate for use as an elementary molecular ligand is the tetrahedral P_4 molecule. P_4 has relatively strong internal π bonds and does not show perfect pairing in the ground state.[3] It is therefore an unsaturated molecule, and the most favorable conditions for bonding to a transition metal atom should be those under which the metal can both accept and back-donate charge density to the P_4 molecule. We therefore examined the reactions of P_4 with low-valent, coordinatively unsaturated group VIII metal complexes. In the present communication we report the characterization of several monomeric, diamagnetic complexes which appear to contain an intact P_4 molecule bonded to a rhodium atom.

(1) L. Vaska, *Science*, **140**, 809 (1963).
(2) J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *J. Amer. Chem. Soc.*, **90**, 5430 (1968).
(3) R. R. Hart, M. B. Robin, and N. A. Kuebler, *J. Chem. Phys.*, **42**, 3631 (1965).

Table I. P_4 Complexes of Rhodium[a]

Compound[b]	Mp, °C[c]	Mol wt[d] Found	Mol wt[d] Required	Other data
$RhCl(P_4)(Ph_3P)_2$	171–173	Not measured		Mass spectrum[i] shows P_4^+ peak
$RhCl(P_4)(m\text{-}Tol_3P)_2$	110–115	765[e]	871	^{31}P nmr[j] d, δ −64.8 ppm (relative to PEt_3), J_{RH-P} = 112 cps; no P_4 lines
$RhCl(P_4)(p\text{-}Tol_3P)_2$	132–134	760,[f] 920[g]	871	
$RhCl(P_4)(Ph_3As)_2$	104–106	700[h]	875	Mass spectrum[i] shows P_4^+ peak

[a] All compounds listed had satisfactory analyses for C, H, P, As, and Cl. [b] Abbreviations: Ph, C_6H_5; *m*-Tol, *m*-$CH_3C_6H_4$; *p*-Tol, *p*-$CH_3C_6H_4$. [c] In evacuated capillary, with decomposition. [d] Measured with a Mechrolab osmometer at 37° in the solvent indicated. Readings were taken at 5-min intervals over a 20-min period and extrapolated to zero time. [e] 33.1 g/l. in C_6H_6. [f] 23.5 g/l. in $CHCl_3$. [g] 1.19 g/l. in C_6H_6. [h] 15.7 g/l. in $CHCl_3$. [i] Determined by Gollob analytical laboratory. [j] In CH_2Cl_2 at $\sim -60°$ with ^1H decoupling; d stands for doublet.

Table II. Selected Vibrational Frequencies (cm^{-1}) of Rhodium–P_4 Complexes[a,b]

P_4[c] Ir	P_4[c] R	Assignment T_d	C_{3v}	C_s	$RhCl(P_4)(Ph_3P)_2$ Ir	$RhCl(P_4)(Ph_3P)_2$ R	$RhCl(P_4)(m\text{-}Tol_3P)_2$ Ir	$RhCl(P_4)(m\text{-}Tol_3P)_2$ R[d]	$RhCl(P_4)(p\text{-}Tol_3P)_2$ Ir	$RhCl(P_4)(p\text{-}Tol_3P)_2$ R	$RhClP_4(Ph_3As)_2$ Ir	$RhClP_4(Ph_3As)_2$ R[f]
	606	$\nu_1(A_1)$ →	A_1 →	A'	569 s	571 w	565 sh		563 s	564 w	566 s	N.o.
461	465	$\nu_2(T_2)$ →	A_1 →	A'	433 s	438 m	*e*		*e*	433 w	428 m	436 w
			E →	A'	387 m	386 s	401 m		*e*	388 m	405 s	390 m
				A''	~376 sh	~374 sh						
	363	$\nu_3(E)$ →	E →	A'	349 w	344 w	N.o.		345 vw?	343 vw?	*e*	N.o.
				A''								
		$\nu(M - Cl)$			276 s	275 s	282 br, s		283 s	277 s	270 s	~275 m

[a] Only nonphosphine (arsine) bands are listed. Ir frequencies above 500 cm^{-1} were measured on pressed CsI disks and below 500 cm^{-1} on Nujol mulls between polyethylene plates. Raman spectra were determined with a Spex Ramalog on polycrystalline samples in evacuated capillaries. The phosphine complexes were excited with the 6471-Å Kr laser line and the arsine complex with the 5682-Å line. [b] Abbreviations: m, medium; s, strong; sh, shoulder; w, weak; br, broad; N.o., not observed. [c] Ir of P_4 in CS_2 solution: H. J. Bernstein and J. Powling, *J. Chem. Phys.*, **18**, 1018 (1950). Raman of liquid phosphorus: C. S. Venkateswaran, *Proc. Indian Acad. Sci., Sect. A*, **2**, 260 (1935); **4**, 345 (1936). [d] Decomposes in laser beam. [e] Obscured by phosphine or arsine ligand absorption. [f] Poor Raman scatterer.

The new compounds have the general formula $RhCl(P_4)L_2$, L = $(C_6H_5)_3P$, $(p\text{-}CH_3C_6H_4)_3P$, $(m\text{-}CH_3C_6H_4)_3P$, $(C_6H_5)_3As$, and were obtained from the reaction of the appropriate tris-*tert*-phosphine (arsine) rhodium halide with white phosphorus in methylene chloride or ether at Dry Ice temperature

$$L_3RhCl + P_4 \xrightarrow[CH_2Cl_2 \text{ or } Et_2O]{-78°} L_2RhCl(P_4)$$

All reactions were carried out under nitrogen in dry, degassed solvents. The preparation of the triphenylphosphine complex is typical. A solution of white phosphorus (70 mg, 0.56 mmol) in dichloromethane[4] (20 ml) was added dropwise, over 15 min, to a solution of tris(triphenylphosphine)chlororhodium(I) (500 mg, 0.54 mmol) in dichloromethane (15 ml) at −78°. After stirring for 45 min at −78°, the color of the reaction mixture had changed from deep red to yellow. Dropwise addition of diethyl ether (*ca.* 200 ml) to the cold solution precipitated a yellow solid. The solid was collected under nitrogen while cold, washed with ether, and dried at 82° (10^{-3} mm) to give 305 mg (72%) of $RhCl(P_4)[(C_6H_5)_3P]_2$. *Anal.* Calcd for $C_{36}H_{30}P_6ClRh$: C, 54.9; H, 3.8; P, 23.6; Cl, 4.5. Found: C, 54.8; H, 4.0; P, 23.5; Cl, 4.7

Table I lists the compounds that have been characterized and some of their properties. The P_4 complexes are all moderately air sensitive but stable in the solid state out of contact with air. They are soluble in benzene, chloroform, and methylene chloride; the latter is the best solvent, and the *m*-tolyl complex is the most soluble (~0.1 *M* at 25°, ~0.02 *M* at −60°). At low temperature (−78°) the solutions are stable for days, but at room temperature they are extensively decomposed in less than 1 hr. However, the solutions were sufficiently stable to permit molecular weight measurements (*cf.* Table I, footnote *d*) which show the P_4 complexes to be monomeric.

There are several pieces of evidence for the presence of an intact P_4 molecule in the new compounds. (1) When the mass spectrum of the triphenylarsine and triphenylphosphine complexes was measured at different temperatures, the former showed a strong P_4^+ peak at 80° and the latter at 150°. No peak due to a rhodium-containing species was observed. (2) The P_4 is easily displaced by carbon monoxide

$$RhCl(P_4)(Ph_3P)_2 + CO \xrightarrow[CH_2Cl_2]{-78°} trans\text{-}RhCl(CO)(Ph_3P)_2$$

Triethylphosphine and 1,2-bisdiphenylphosphinoethane displace both P_4 and triphenylphosphine

$$RhCl(P_4)(Ph_3P)_2 + Et_3P \xrightarrow[CH_2Cl_2-Et_2O]{\sim -78°} Rh(Et_3P)_3Cl + [Rh(Et_3P)_2Cl]_2$$

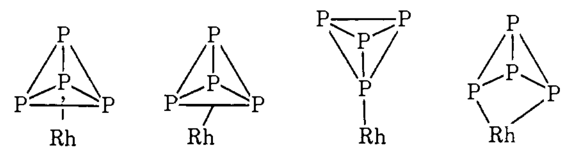
$$RhCl(P_4)(Ph_3P)_2 + Ph_2PCH_2CH_2PPh_2 \xrightarrow[CH_2Cl_2]{-78°} [Rh(Ph_2PCH_2CH_2PPh_2)_2]Cl$$

Ethylene and hydrogen do not react at −78°. (3) The infrared and Raman spectra show bands attributable to a bound P_4 molecule under C_{3v} or C_s symmetry. This is illustrated by Table II in which the infrared and Raman spectra of free P_4 are compared with the bands attributed to P_4 in the complexes. Assignment of a band as a nonphosphine (arsine) frequency is based on

(4) The phosphorus was freshly cut from the center of a stick, washed with water, and dried at 10^{-3} mm for *ca.* 20 min; it was then dissolved in dichloromethane under nitrogen.

comparison with the spectrum of the $RhClL_3$ starting material and related compounds. The highest energy nonphosphine (arsine) band is assumed to correspond to the 606-cm^{-1} $\nu_1(A_1)$ mode of P_4. The $\nu_2(T_2)$ frequency of free P_4 (465 cm^{-1}) splits into an A_1 and an E mode under C_{3v} symmetry, and we assign the next two lower nonphosphine (arsine) bands to these vibrations. In the triphenylphosphine complex, the lowest of these two vibrations (386 cm^{-1}) has a shoulder, and we therefore attribute it to the E mode split either by solid state effects or reduced molecular symmetry. The $\nu_3(E)$ frequency of P_4 (363 cm^{-1}) remains unsplit under C_{3v} symmetry; we assign the next lower nonphosphine (arsine) band to this vibration. The frequencies assigned to bound P_4 are from 15 to 90 cm^{-1} lower in energy than the corresponding frequency in free P_4.

A–D show the possible ways in which P_4 may be linked to the metal atom. We consider D to be unlikely because of the ease with which P_4 is displaced



A B C D

from the complex by CO, and because we expect that breaking one of the edge bonds of the P_4 tetrahedron would give rise to a greater perturbation of the P_4 vibrational spectrum than is observed. We also consider C to be unlikely because the P_4 molecule has no lone-pair p electrons.[3,5,6] Of the remaining two possibilities we favor A, bonding through a face, over B, bonding through an edge. The P_4 valence-shell electrons are in orbitals of symmetry A_1, E, and T_2. Under C_s symmetry (the overall molecular symmetry for A or B) these orbitals become, respectively, A', $(A' + A'')$, and $(2A' + A'')$, all of which can overlap with empty metal orbitals. In addition, the lowest lying empty P_4 orbitals, T_1 and T_2, become, respectively, $(A' + 2A'')$ and $(2A' + A'')$; all of these can overlap with filled metal d orbitals.

Attempts to obtain structural information from ^{31}P nmr spectra have so far been unsuccessful; the *m*-tolyl complex in CH_2Cl_2 at $\sim -60°$ with ^1H decoupling does not show any ^{31}P nmr lines that may be attributed to P_4. At δ −64.8 ppm (relative to $P(C_2H_5)_3$) is an apparently structureless phosphine line which is split into a doublet by coupling with the rhodium (J_{Rh-P} = 112 cps). Each member of the doublet has a width at half-height of ~30 cps. The failure to observe ^{31}P nmr lines due to P_4 in the complex, and the apparent absence of P–P coupling while Rh–P coupling is present, suggests that the P_4 is undergoing either inter- or intramolecular exchange. The nmr results indicate that the phosphine ligands are equivalent.

Acknowledgment. We thank Dr. F. N. Tebbe for arranging to have the ^{31}P nmr spectra determined at the Du Pont Co. Central Research Laboratory.

(5) S. F. A. Kettle, *Theoret. Chim. Acta*, **4**, 150 (1966).
(6) R. M. Archibald and P. G. Perkins, *Chem. Commun.*, 569 (1970).

A. P. Ginsberg,* W. E. Lindsell
Bell Telephone Laboratories, Incorporated
Murray Hill, New Jersey 07974
Received January 15, 1971

Hydrolysis of Acetals and Ortho Esters. Specific Salt Effects Associated with Buffer Experiments in Mixed Solvents

Sir:

We report here some experimental results on specific salt effects which have a close bearing on the study of general acid catalysis in the hydrolysis of acetals and ortho esters.[1] Surprisingly, in this particular context, the presence or absence of the specific effects has not been studied before drawing conclusions.

The inadequacy of the ionic strength principle was clearly demonstrated by Olson and Simonson[2] for equilibria and kinetics of ionic reactions in water. Significant implications for reactions dealt with in this communication follow from the extensive studies of Grunwald and coworkers.[3] They not only derived exact thermodynamic equations for salt effects in mixed solvents, but also devised simple methods, based on linear free energy correlations, for the treatment of experimental data obtained with different salts.

Our point is the following. In order to detect possible involvement of general acid catalysis, one traditionally makes a series of rate measurements in buffer solutions of constant ionic strength and constant buffer ratio, $(HA)/(A^-)$. When varying the concentration of the Brønsted acid, (HA), the ionic strength constancy is maintained with some added electrolyte. Ordinarily, it is thus implicitly assumed that all the activity coefficients involved are influenced by the ions derived from the buffer components in the same way as by those of the added electrolyte. Yet, the validity or invalidity of this assumption, that is, the absence or presence of specific salt effects, can be experimentally established if using different electrolytes to make up the desired overall ionic strength.

The above point is illustrated by the results shown in Figure 1. As an example, we have chosen the hydrolysis of triethyl orthobenzoate, as a very similar reaction; the hydrolysis of trimethyl orthobenzoate in 70% methanol–water solvent,[4] has been reported to be subject to general acid catalysis. From the slope of line A alone, $(1.23 \pm 0.13) \times 10^{-2}$ M^{-2} sec^{-1}, obtained with sodium chloride as the added electrolyte, one might be tempted to assume the presence of general acid catalysis by the undissociated acid with a catalytic coefficient of this magnitude. However, as seen from the slopes of lines B and C, quite different results—even of different sign—are obtained when using electrolytes other than sodium chloride.

The observed variations in the hydrolysis rates can be accounted for in terms of specific salt effects on the hydronium ion catalysis. For the second-order rate coefficient of this reaction (first-order coefficient

(1) (a) E. H. Cordes, *Progr. Phys. Org. Chem.*, **4**, 1 (1967); (b) T. H. Fife and L. K. Jao, *J. Amer. Chem. Soc.*, **90**, 4081 (1968); (c) R. H. DeWolfe, K. M. Ivanetich, and N. F. Perry, *J. Org. Chem.*, **34**, 848 (1969); (d) A. Kankaanperä and M. Lahti, *Acta Chem. Scand.*, **23**, 2465 (1969); *Suom. Kemistilehti B*, 105 (1970); all these articles contain numerous references to the pertinent literature.
(2) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 348, 1167, 1322 (1949).
(3) (a) E. Grunwald and A. F. Butler, *J. Amer. Chem. Soc.*, **82**, 5647 (1960); (b) R. F. J. Duynstee, E. Grunwald, and M. L. Kaplan, *ibid.*, **82**, 5654 (1960); (c) E. Grunwald, G. Baughman, and G. Kohnstam, *ibid.*, **82**, 5801 (1960), and references to earlier studies therein.
(4) H. Kwart and M. B. Price, *ibid.*, **82**, 5123 (1960).