rich), and the early-transition-metal alkoxides (Alfa) were reagent grade materials used as received. The 90-MHz ^{1}H NMR spectra were obtained on a Varian EM390 spectrometer while 61.4-MHz ^{2}H NMR spectra were measured on a Bruker WM 400 instrument. GC–mass spectrometric studies were conducted by using a Varian Model 3700 GC interfaced with a Du Pont Model 491 mass spectrometer. Electron-impact studies were carried out at 70 eV ionizing voltage while chemical-ionization studies utilized isobutane as reagent.

β-Exchange Studies. Typical Run. A Carius tube of ca. 5-mL volume was charged with ethanol-*d* (2.45 g, 50 mmol), and the transition-metal ethoxide catalyst (1.0 mg-atom metal). The tube was frozen in liquid nitrogen and evacuated on a vacuum line. After three freeze–pump–thaw cycles the tube was sealed with a torch. Sets of four tubes were placed in a stainless-steel autoclave, which was half-filled with hexane to equalize the pressure during heating. The autoclave was maintained at the indicated temperature (usually 200 °C) for 14 h. Cooled tubes were opened in a nitrogen-filled glovebox. Total H–D exchange was determined by integrating the OH resonance vs. the methylene resonance in the 90-MHz ^{1}H NMR spectrum. (Neat material was required to avoid overlap of these resonances which occurred on dilution.) The 61.4-MHz ^{2}H NMR spectrum was then examined; the integration of the resonances at δ 0.98, 0.96, and 0.94 gave the relative amount of mono-, di-, and trideuteriated ethanol, respectively.

α-Exchange Studies. The reaction was carried out as above except that the ethanol-*d* was replaced with a 1:1 mixture of ethanol and ethanol-*1,1,*-d_2. The resultant ethanol was then analyzed by electron-impact GC–MS, correcting for the isotopic distribution of the starting mixture of alcohols. In a typical run (220 °C, 40 h, 0.25 M tantalum ethoxide catalyst) the conversion to monodeuteriated alcohol was 4%. Alternatively, heating a 1:1 (volume) mixture of ethanol-*1,1*-d_2 and 0.3 M metal octoxide in 1-octanol for 80 h at 220 °C followed by fractional distillation gave the following levels of ^{1}H incorporation into the methylene group by NMR: 33% (Ta); 11% (Zr). In appropriate control reactions, the methylene ^{1}H NMR resonance was 2%, consistent with the isotopic purity (98%) of the starting alcohol.

Racemization of 2-Butanol. In a typical run, heating of a 1:1 (volume) mixture of (*R*)-(−)-2-butanol and 0.3 M zirconium octoxide in 1-octanol at 220 °C followed by fractional distillation afforded 2-butanol with $[\alpha]_D^{25}$-6.3 ± 0.2° (20 h) and −3.0 ± 0.1° (40 h). A control containing no catalyst after 20 h at 220 °C gave −12.4 ± 0.2°, essentially identical with that of the starting alcohol (−12.5 ± 0.2°).

Preparation of Labeled 4-*tert*-Butylcyclohexanols. Commercial *tert*-butylcyclohexanol as received was a 70:30 mixture of trans and cis material. Flash chromatography of a 5.0-g sample in 30% ethyl acetate and 70% hexane following the general procedure of Still[10] afforded from cuts 11–13 the cis isomer (1.15 g) and from cuts 15–20 the trans isomer (2.85 g). The purified alcohols were *O*-deuteriated by repeated treatment with excess ethanol-*d* followed by distillation of the ethanol in vacuo.

Exchange Studies with 4-*tert*-Butylcyclohexanol-*d*. Tubes were charged as above with *trans*-4-*tert*-butylcyclohexanol-*d* (0.75 g), ethanol-*d* (0.75 g), and metal alkoxide catalyst (0.15 g). The mixture was heated for 14 h at 220 °C. The cooled solutions were added to water (50 mL), extracted with ether (50 mL), and dried ($MgSO_4$). Removal of the solvent afforded a white solid, which was *O*-silylated by stirring a sample (0.1 g) overnight with excess (0.5 g) (dimethylamino)trimethylsilane in toluene (2 mL). The products were analyzed by GC–MS. The extent of isomerization was 9.2% (Ta catalyst) and 5.5% (Zr catalyst). In each case molecular ion for the cis silyl ethanol was observed at *m/e* 231 and 232 (roughly 1:1). In contrast, an authentic sample of silylated starting material showed only *m/e* 228. The large M − 15 peaks at *m/e* 213 (authentic unlabeled alcohol) and at *m/e* 216 and 217 (reaction products) further corroborated this result.

Acknowledgment. We thank Professor George M. Whitesides for helpful discussions.

Registry No. *cis*-**3**, 937-05-3; *trans*-**3**, 21862-63-5; *trans*-**3**-*O*-*d*, 104778-37-2; *cis*-**3**-*O*-*d*, 104778-41-8; *trans*-**3** (trimethylsilyl ether, unlabeled), 32147-25-4; *cis*-**3** (trimethylsilyl ether, unlabeled), 32147-26-5; *cis*-**3**-*O*-*d* (β-trideuteriated), 104778-38-3; *cis*-**3** (trimethylsilyl ether, β-trideuteriated), 104778-39-4; *cis*-**3** (trimethylsilyl ether, β-tetradeuteriated), 104778-43-0; CH_3CH_2OD, 925-93-9; CH_3CHO, 75-07-0; $Ta(OEt)_5$, 6074-84-6; $Zr(OEt)_4$, 18267-08-8; $Ta[CH_3(CH_2)_7O]_5$, 104778-40-7; $Zr[CH_3(CH_2)_7O]_4$, 7449-59-4; CH_3CD_2OH, 1859-09-2; CH_2DCH_2OD, 74902-54-8; CD_2HCH_2OD, 104778-42-9; CD_3CH_2OD, 22593-50-6; $Ti(OEt)_4$, 3087-36-3; $Nb_2(OEt)_{10}$, 18533-41-0; $W(OEt)_6$, 62571-53-3; Et_3N, 121-44-8; C_5H_5N, 110-86-1; H_2, 1333-74-0; (*R*)-(−)-2-butanol, 14898-79-4; (±)-2-butanol, 15892-23-6.

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Contribution from the Department of Chemistry,
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Reactions of HCl(g), DCl(g), and HBr(g) with the Adduct Pyrazine–Phosphorus(V) Chloride

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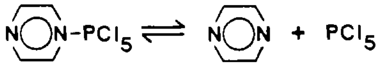
In previous communications we have reported the synthesis, molecular structure, and solution properties of the acid–base adduct formed from pyrazine (pz), $C_4H_4N_2$, and phosphorus(V) chloride, PCl_5.[1,2] In the solid state the molecule, pz·PCl_5, belongs to point group C_{2v} with octahedral geometry around phosphorus. The plane of the pyrazine ring bisects the Cl–P–Cl 90° angle, and the P–N bond is unusually long, 2.021 Å. In solution of nitromethane, the adduct is in equilibrium with PCl_5 and pz.



(1)

This rapid exchange is responsible for a singlet in the ^{1}H NMR spectrum, even at −100 °C.

Because a second nitrogen base site on the adduct is available for further reaction, we have investigated the possibility of coordinating a second mole of acid to the adduct. Lever, Lewis, and Nyholm have reported the addition of 2 mol of BCl_3 to pz, yielding a stable compound,[3] but we find no evidence of a reaction of pz with a second mole of PCl_5. This could be due to a combination of reduced acidity and/or more severe steric requirements of PCl_5 compared to BCl_3. In this communication we report reactions between pz·PCl_5 and the acids HCl(g), DCl(g), and HBr(g). Reactions were performed in a *dispersive* medium, rather than in solution, to avoid the influence of the equilibrium of eq 1.

Experimental Section

Materials. Experiments were performed on a standard vacuum line,[4] employing a mercury diffusion pump and a CO_2-calibrated, U-trap system for gas measurements and trap-to-trap fractionation.

Pz·PCl_5 was synthesized as has been described elsewhere.[1,2] Purification was achieved by vacuum sublimation at 60–64 °C. The pyridine (py) adduct py·PCl_5 was synthesized and purified in a manner analogous to that for pz·PCl_5. Anal. Calcd for $C_5H_5NPCl_5$: Cl, 61.69; P, 10.78. Found: Cl, 60.63; P, 10.72.

Hydrogen chloride gas (Matheson) was used after several fractionations through a −96 °C U-trap. The purity was checked by infrared spectroscopy utilizing a 10-cm gas cell fitted with NaCl windows.

Two sources of hydrogen bromide were used: (i) from the bromination of toluene in the vacuum system, and (ii) from Airco. Purification and identification were achieved in the same manner as for HCl.

Deuterium chloride was prepared from freshly sublimed PCl_5 and 99.96 atom % D_2O (Aldrich).[5]

Carbon tetrachloride and methylene chloride were each stirred for several days over P_4O_{10}, distilled, and stored in an inert-atmosphere glovebox.

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(5) Great difficulty was encountered in obtaining a clean infrared spectrum of DCl, free of HCl. It was determined that the major source of HCl was due to H–D exchange from moisture in the KBr or NaCl windows of the IR cell. Once DCl was introduced into the IR cell, the relative intensity of the HCl band at 2880 cm^{-1} increased with time as the DCl band at 2080 cm^{-1} decreased. The use of new o-ring seals and heating of the salt plates to 400 °C, under vacuum, reduced significantly the amount of H–D exchange, yielding minimum HCl production in the IR cell. In addition, the vacuum line and the IR cell were both exposed to D_2O vapors for several hours after the heat treatments. Thereafter, additional flaming of the vacuum system followed by pumping was used to insure minimal availability of adsorbed H_2O in the system.

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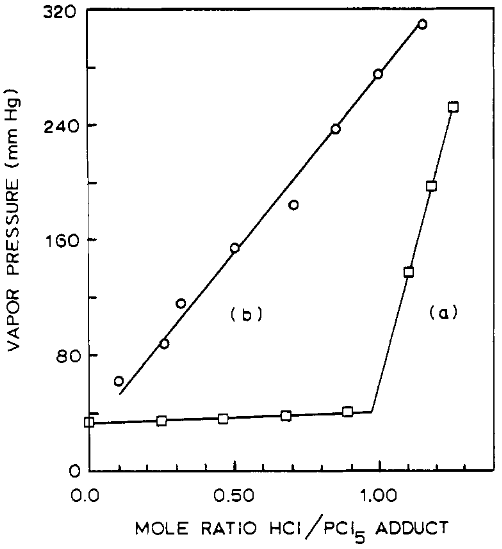


Figure 1. Tensimetric titration of (a) $pz{\cdot}PCl_5$ and (b) $py{\cdot}PCl_5$ with HCl(g) in CCl_4 at 0 °C.

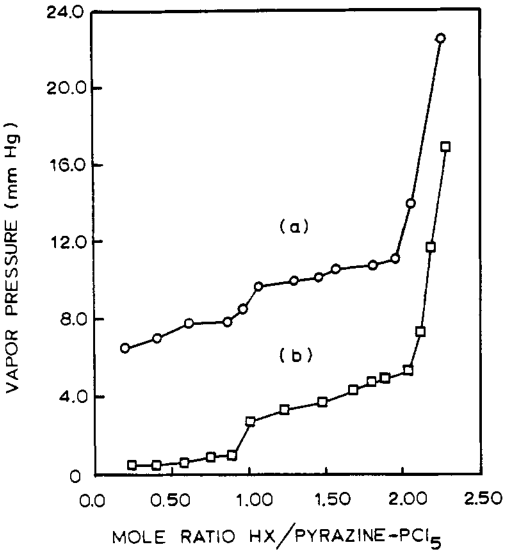


Figure 2. Tensimetric titration of $pz{\cdot}PCl_5$ with (a) HCl(g) and (b) HBr(g) in CH_2Cl_2 at −63 °C.

Methods. In a typical tensimetric titration, an accurately weighed solid sample of 4–10 mmol of $pz{\cdot}PCl_5$ was placed into a tensimeter[4,6] along with 10 mL of either CCl_4 or CH_2Cl_2. The mix was degassed by at least three freeze–pump–thaw cycles. Approximately equal portions of HX gas were added to the tensimeter from the calibrated trap system after the previous addition had been allowed to reach vapor pressure equilibrium (about 45 min). The slush baths were frequently stirred and replenished to maintain a temperature range of ±1 °C.

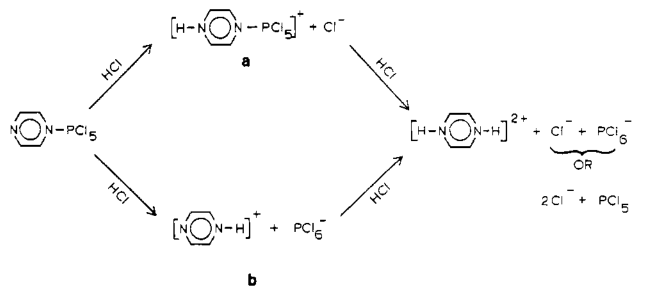
^1H NMR spectra were recorded on a Perkin-Elmer R24A spectrometer operating at 60 MHz and ambient temperature with CH_3NO_2 as solvent and Me_4Si as internal standard.

Infared spectra of Nujol and Fluorolube mulls were recorded on a Perkin-Elmer 283 spectrophotometer. Within the time required for recording the spectrum, significant hydrolysis was not observed.

The Raman spectrum was recorded with a SPEX 1401 double monochrometer between 100 and 700 cm^{-1} on a sample of $pz{\cdot}PCl_5{\cdot}HCl$ that had been sealed in a melting point capillary tube under nitrogen. The 457.9-nm line of an Ar ion laser was slit focused with a cylindrical lens for use with a 135° back-scattering technique. A sweep rate of 1 cm^{-1}/s was employed with slits of 400, 500, 500, and 400 μm.

X-ray powder diffraction samples were prepared by flame sealing inside a 0.5-mm glass capillary tube. Diffraction patterns were recorded photographically with a Debye-Scherrer camera of 114.6-mm diameter and Cu radiation.

Scheme I



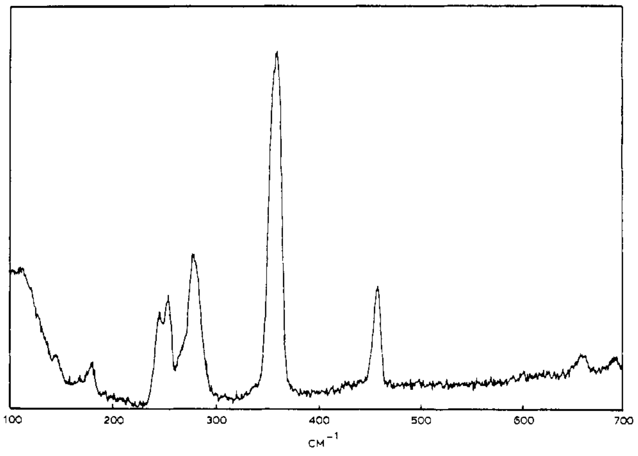


Figure 3. Raman spectrum of powdered $pz{\cdot}PCl_5{\cdot}HCl$.

Results and Discussion

(1) Reaction of HCl(g) with $pz{\cdot}PCl_5$. Tensimetric titrations, performed at 0 °C in CCl_4 and at −63 °C in CH_2Cl_2, yielded different results (Figures 1a and 2a). At 0 °C the titration plot indicates the formation of a 1:1 complex, $pz{\cdot}PCl_5{\cdot}HCl$. At −63 °C, two complexes are formed, $pz{\cdot}PCl_5{\cdot}HCl$ and $pz{\cdot}PCl_5{\cdot}2HCl$. Both products are white solids, but, upon warming, the 2:1 solid liberates 1 equiv of HCl. X-ray powder diffraction patterns, recorded at room temperature, are identical for both the 0 °C and −63 °C reaction products. This result is not surprising because pyrazinium dihydrochloride also loses 1 mol of HCl at room temperature.

The ^1H NMR spectrum of the monoprotonated complex, $pz{\cdot}PCl_5{\cdot}HCl$, recorded at room temperature in nitromethane solvent, exhibits singlet resonances at 9.20 and 16.6 ppm with relative intensities 4:1. The chemical shift of the weaker resonance changes with concentration, as expected for an acidic proton.

Two paths are possible to account for these observations. Path a in Scheme I is suggested by the availability of the second nitrogen base site on pz. Path b in Scheme I follows from a report that, *in solution*, the mixture of py, PCl_5, and HCl yields pyridinium hexachlorophosphate.[7] The experiments reported below distinguish between parts a and b of Scheme I by identifying the product of the first step.

NMR Spectroscopy. The chemical shifts of the pyrazine ring protons of pz (8.62 ppm), $pz{\cdot}HCl$ (9.08 ppm), $pz{\cdot}PCl_5$ (9.17 ppm), and $pz{\cdot}PCl_5{\cdot}HCl$ (9.20 ppm) increase with the degree of coordination. Rapid exchange (eq 1) accounts for a single, average resonance position for these hydrogen atoms. If path a in Scheme I was operative, the resonance position of $pz{\cdot}PCl_5{\cdot}HCl$ would resemble that of $pz{\cdot}HCl$. The larger chemical shift value of $pz{\cdot}PCl_5{\cdot}HCl$ compared to that of $pz{\cdot}HCl$ argues for pz exchanging

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with both H^+ and PCl_5 (path a in Scheme I).

Tensimetric Titration. A tensimetric titration was performed on py·PCl_5 under conditions identical with those used for pz·PCl_5. (Compare parts a and b of Figure 1.) The failure of py·PCl_5 to react with HCl indicates that P–N bond rupture is probably not the mechanism by which pz·PCl_5 reacts with the first mole of HCl under heterogeneous conditions.

Raman Spectroscopy. The Raman spectrum of pz·PCl_5·HCl, recorded between 100 and 700 cm^{-1} is shown in Figure 3. Bands at 183, 362, and 460 cm^{-1} are pertinent to this discussion when compared to the spectra of pz·PCl_5[2] and py·PCl_5.[8] The a_1 ν(P–N) bands of these two compounds appear at 189 and 190 cm^{-1}, respectively. Because of similar relative intensity, we assign the 183 cm^{-1} band to the P–N mode of pz·PCl_5·HCl. Both pz·PCl_5 and py·PCl_5 display Raman bands at 351 (strongest band, a_1 $\nu(P–Cl_{eq})$) and 455 cm^{-1} (a_1 $\nu(P–Cl_{ax})$). Pz·PCl_5·HCl has two Raman bands of similar relative intensities at 362 (strongest band) and 460 cm^{-1}, which we assign to a_1 $\nu(P–Cl_{eq})$ and a_1 $\nu(P–Cl_{ax})$. The presence of these modes, and the fact that neither PCl_6^- [9] nor pyrazinium ion[10] display the same Raman pattern, argues in favor of part a in Scheme I.

Infrared Spectroscopy. Comparison of the spectra of pz·PCl_5·HCl and pz·PCl_5·DCl shows the following. pz·PCl_5·HCl has a band at 2110 cm^{-1} (broad), which is shifted to 1590 cm^{-1} in its deuteriated analogue. The frequency ratio $\nu(N–D)/\nu(N–H)$ of 0.754 compares favorably with 0.768 for the deuterium-shifted N–H(D) band observed for pz·$H(D)^+Cl^-$ by Foglizzo and Novak.[10] Their infrared absorptions are at 2800 (N–H) and 2150 cm^{-1} (N–D). Our lower frequencies can be attributed to the decreased basicity of the second ring nitrogen. In the adduct, $[(D)H–NC_4H_4N·PCl_5]^+$, the N–H(D) bond para to the N–P bond would be expected to exhibit a reduced N–H(D) stretching frequency compared to that of monoprotonated pyrazine. This is consistent with the pK_a values of 0.65 and –5.78 for the mono and diacid forms of pyrazine[11] and supports the contention that the species $[H–NC_4H_4N·PCl_5]^+$ is present as postulated in the first step of path a of Scheme I.

(2) Reaction of HBr(g) with pz·PCl_5. Tensimetric titrations performed with HBr(g) yielded results parallel to the HCl reactions discussed above. (Figure 2b) The diprotonated adduct is not stable at room temperature, similar to the HCl addition product. However, a change in the color of the reaction mix occurred upon adding HBr(g) to pz·PCl_5. The chemistry responsible for the color change did not affect the tensimetric titration result, except that recovery of gas, added beyond a 2:1 mole ratio of HBr/pz·PCl_5, showed a quantitative excess of HCl, not HBr. A metathesis reaction occurs, which yields PBr_5 and HCl and is the subject of current investigation.

Conclusions

Under the conditions employed in these experiments (heterogeneous reaction between undissolved pz·PCl_5 and HX in CCl_4 and CH_2Cl_2), protonation of the para nitrogen atom of the pyrazine ring takes place. The attack of HX occurs in this manner, rather than to displace PCl_5 from the complex. The analogous complex, py·PCl_5, was found not to react with HX under conditions identical with those employed with pz·PCl_5. The P–N bond, although labile in these complexes when in solution, is inert to attack of the first mole of HX under the conditions reported herein.

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Comparative Matrix Isolation and Time-Resolved Infrared Studies on the Photochemistry of $MnRe(CO)_{10}$ and $Re_2(CO)_{10}$: Evidence for CO-Bridged $MnRe(CO)_9$

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Received June 2, 1986

We wish to report the results of an investigation into the photochemistry of $MnRe(CO)_{10}$ and $Re_2(CO)_{10}$ using both matrix isolation at 12 K and time-resolved IR spectroscopy of solutions at room temperature. For both molecules we have detected primary photoproducts involving loss of CO from the parent decacarbonyl. $MnRe(CO)_9$ has a bridging CO group while $Re_2(CO)_9$ does not. In hydrocarbon solution, $MnRe(CO)_9$ reacts with CO substantially faster than does $Mn_2(CO)_9$.

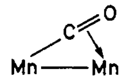
The photochemistry of organometallic compounds[1] has been extensively studied, and at present considerable interest is centered on dinuclear systems possessing metal–metal bonds.[2] However, only recently has it been recognized that there are two primary photochemical pathways for such compounds: (i) homolytic cleavage of the metal–metal bond to give radicals or (ii) dissociative loss of CO without rupture of the metal–metal bond. Evidence for these processes came originally from UV flash photolysis kinetic studies, which did not, however, provide much structural information about the intermediates. Definitive identification of these intermediates has required time-resolved IR spectroscopy, which in turn has made extensive use of IR data from matrix isolation experiments for interpretation of the spectra.[3]

A particularly well-studied problem is the photolysis of $Mn_2(CO)_{10}$, where conventional flash photolysis,[4] matrix isolation,[5,6] and time-resolved IR spectroscopy[7,8] have all been used. The two primary photochemical processes are

$$Mn_2(CO)_{10} \rightarrow 2Mn(CO)_5$$

$$Mn_2(CO)_{10} \rightarrow Mn_2(CO)_9 + CO$$

Detailed matrix isolation experiments[5,6] have shown that the CO-loss product $Mn_2(CO)_9$ has a novel structure involving an η^1, η^2 semibridging CO group (**1**).



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By comparison with $Mn_2(CO)_{10}$, relatively less is known about the photochemistry of $Re_2(CO)_{10}$. Two recent flash photolysis studies, one with UV detection[9] and the other with IR spectroscopy,[10] have shown that the $Re_2(CO)_{10}$ system is more complex than that of $Mn_2(CO)_{10}$ and that there is no evidence for a CO-bridged $Re_2(CO)_9$ species in solution.[10] Even less is known about the photochemistry of the mixed-metal carbonyl $MnRe(CO)_{10}$.

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