the asymmetric Cl_3^- ion in benzene solution in the presence of tetra-*n*-butylammonium cation.[18]

The reaction of KCl and HCl produced a very intense band at 736 cm^{-1} and a weak absorption at 682 cm^{-1}. The ν_3 antisymmetric vibration of linear, symmetric HCl_2^- in crystals with large cations has been observed in this spectral region,[19] and matrix-isolated $M^+HCl_2^-$ should give a similar absorption. The 736-cm^{-1} band is, therefore, assigned to ν_3 of HCl_2^- in the $K^+HCl_2^-$ species; the weaker 682 cm^{-1} feature is presumably due to the same species in a different matrix site. The 736-cm^{-1} band shifted to 498 cm^{-1} when DCl was employed. The intense doublet in Figure 1 indicates that only a single hydrogen is involved in the vibration, which supports the assignment to HCl_2^-. Also, the H/D frequency ratio is 1.48, while the anticipated harmonic ratio is only 1.41. This is due to dominance of the anharmonicity by a positive quartic term in the potential function, and the absence of a cubic term, which requires a linear, centrosymmetric structure for the HCl_2^- species, as discussed by Noble and Pimentel.[1] Raman spectra of the $Rb^+HCl_2^-$ species produced a weak, reproducible signal at 250 cm^{-1}.[11] This band, attributed to ν_1 of HCl_2^-, is near the 260-cm^{-1} value deduced from the 956-cm^{-1} assignment to $\nu_1 + \nu_3$ of isolated HCl_2^-.[2]

It is clear that the 736-cm^{-1} band observed from the reaction of KCl with HCl is due to ν_3 of HCl_2^- in $K^+HCl_2^-$ with a linear symmetric geometry for the anion. The band assigned to ν_3 of the HCl_2 radical by Noble and Pimentel[1] was observed at 696 cm^{-1}, and the same band was assigned to the HCl_2^- anion by Milligan and Jacox.[2] While the $M^+HCl_2^-$ frequencies listed in Table I do not exactly match their observed frequency, the agreement is substantial, and we must conclude that the band at 696 cm^{-1} in these earlier works was in fact due to the isolated HCl_2^- anion. Noble and Pimentel formed this species using a microwave discharge, and it is apparent that the position of their discharge tube led to the trapping of ionic species. In fact, recent quantum mechanical calculations predict linear symmetric FHF to be unstable and infer that ClHCl is likewise unstable.[20]

Reactions of salt molecules and hydrogen chloride in argon matrices have led to the HCl_2^- anion in the species $M^+HCl_2^-$. Comparison of the ν_3 frequencies and deuterium shifts observed here and those observed in microwave and photolysis work has led to the conclusion that the species assigned to the HCl_2 radical by Noble and Pimentel[1] is in fact the isolated anion HCl_2^-, as assigned by Milligan and Jacox.[2] Similar salt-chlorine reactions have produced the $M^+Cl_3^-$ species and identified ν_3 of the trichloride anion. It is clear that the salt-molecule matrix reaction, in essence an ion-molecule reaction, is an effective method of preparing polyatomic ionic molecules for spectroscopic study.

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Unusually Large Platinum–Phosphorus Coupling Constants in Platinum(0) Tetraphosphine Complexes

Sir:

Owing to the tendency of $Pt(PR_3)_4$ compounds (R = aryl or alkyl groups) to dissociate in solution and to the synthetic difficulties of preparing mixed complexes of the type $Pt(PR_3)_2(PR'_3)_2$, very little data are available in the literature concerning the magnitudes of Pt–P and P–P couplings for platinum(0) complexes.[1] Using the triphosphine ligand $CH_3C(CH_2PPh_2)_3$, we have isolated and characterized a series of *dissociatively stable* platinum(0)-tetraphosphine complexes of the type Pt(triphosphine)PR_3.[2]

For these complexes the Fourier transform ^{31}P pattern is essentially first order and consists of a doublet (intensity 3) with platinum-195 satellites and a quartet (intensity 1) with its platinum satellites. The Pt–P coupling observed for the triphosphine ligand (Table I) decreases systematically from 3098 ± 2.4 to 2867 ± 2.4 Hz as the monodentate phosphine changes from $(p\text{-tolyl})_3P$ to PF_3, whereas the Pt–P coupling for the monodentate phosphine increases dramatically in the series $PPh_3 < P(OCH_2)_3CCH_3 < PF_2NMe_2 < P(OPh)_3$. The magnitudes of the Pt–P couplings for the monodentate phosphines are approximately *double* the Pt–P values observed in trans Pt(II) complexes and approximately *55%* larger than the Pt–P couplings in *cis*-$PtCl_2(PR_3)_2$ complexes of the corresponding PR_3 phosphines.[1] Although there are few examples available for direct comparison of the Pt–P and P–P couplings in Pt(II) and Pt(0) complexes of the same ligand, the data for the Me_2NPF_2 complex illustrate the increased Pt–P couplings to the monodentate ligand in our mixed Pt(triphosphine)(PR_3) compounds. The Pt–P coupling in *cis*-$PtCl_2(PF_2NMe_2)_2$ is ~5690 Hz,[3] whereas the Pt–P coupling in Pt(triphosphine)(PF_2NMe_2) is 8838 Hz. Also, the $^2J_{P-P}$ values are considerably larger than found in *cis*-$PtCl_2(PR_3)_2$ complexes. The larger coupling constants do not arise from the different oxidation state of platinum, as the $^1J_{Pt-P}$ and $^2J_{Pt-F}$ values for $Pt(PF_3)_4$ are 6480 and 421 Hz, respectively.[3]

In the few cases where the same PR_3 ligand has been used on both zero-valent platinum and tungsten, a plot of $^1J_{Pt-P}$ against $^1J_{W-P}$ is nearly linear.[4] For example, the phosphite and PF_3 complexes always exhibit the largest values of $^1J_{M-P}$ and $^2J_{P-M-P}$ within their respective series. Except for the ligand Me_2NPF_2, the increasing $^2J_{P-P}$ values are linearly related to the increasing values of $^1J_{Pt-P}$. Unusual $^2J_{P-P}$ values have been observed previously[4-6] for a number of phosphine ligands containing dialkylamino groups.

Using the complex $Pt(Ph_2PCH_2CH_2CH_2PPh_2)_2$[2] (which has four equivalent nonexchanging phosphorus nuclei over

Table I. Pt–P and P–P Coupling Constants for Pt(0) Complexes

Complex	$^1J_{\text{Pt-P}}$, Hz[a,b]	$^2J_{\text{P-P}}$, Hz[b]	$^1J_{\text{Pt-P}}$, Hz[b,c]
Pt(biphos)$_2$[d]	3644	~0	
Pt(triphos)PPh$_3$[e]	3096	51	5400
Pt(triphos)P-(*p*-tolyl)$_3$	3098	51	5380
Pt(triphos)PPh$_2$Me	3075	51	5370
Pt(triphos)P(OCH$_2$)$_3$-CCH$_3$	2990	68	6787
Pt(triphos)PF$_2$NMe$_2$[f]	2893	83	8838
Pt(triphos)P(OPh)$_3$	2883	87	9150
Pt(triphos)PF$_3$[g]	2867	95	*h*
Pt(triphos)CO	2837		

[a] For the "mixed" complexes, the Pt–P coupling constant of the tridentate ligand $CH_3C(CH_2PPh_2)_3$. [b] Resolution is 2.4 Hz. [c] For the "mixed" complexes, the Pt–P coupling constant of the monodentate phosphine. [d] biphos is $Ph_2PCH_2CH_2CH_2PPh_2$. [e] triphos is $CH_3C(CH_2PPh_2)_3$. [f] The $^1J_{\text{P-F}}$, $^2J_{\text{Pt-F}}$, $^3J_{\text{P-F}}$ couplings are 1111.3, 639.7, and 43.0 ± 1 Hz, respectively. [g] The $^1J_{\text{P-F}}$, $^2J_{\text{Pt-F}}$, $^3J_{\text{P-F}}$ couplings are 1321, 895, and 46.4 ± 2.4 Hz, respectively. [h] The very low solubility of this complex has to date prevented direct observation of the platinum-195 satellites. An extrapolated value of 9500 Hz for $^1J_{\text{Pt-P}}$ is obtained from the linear plot of $^1J_{\text{Pt-P(triphos)}}$ vs. $^1J_{\text{Pt-P(mono)}}$ for the other monophosphine ligands.

the temperature range −50 to +60°) as a comparison standard with $^1J_{\text{Pt-P}} = 3644 \pm 2.4$ Hz, the $^1J_{\text{Pt-P}}$ values for the triphosphine are significantly smaller, whereas the $^1J_{\text{Pt-P}}$ values for the monodentate phosphines are much larger. Since the magnitude of the directly bonded coupling constant $^1J_{\text{Pt-P}}$ is dominated by the Fermi contact term,[1] changes in the magnitude of $^1J_{\text{Pt-P}}$ with phosphine within a series of platinum–phosphine complexes are largely dependent[7] on changes in $|S_{\text{P}}(0)|^2$ and α_{P}^2. Thus, the large difference in Pt–P coupling constants observed in our Pt(triphos)PR$_3$ complexes must be related to differences in the two types of Pt–P bonds, in particular to significantly different values of α_{Pt}^2. As the triphosphine ligand restricts the P–Pt–P angles to about 93–94°,[8-11] those three Pt–P bonds will have a smaller s character than "tetrahedral" Pt–P bonds. Thus, the remaining Pt–P bond will be hybridized to include more s character, and would be expected to exhibit a larger coupling constant. The $^1J_{\text{Pt-P}}$ values in Table I provide support for such a rehybridization and redistribution of s character, since the $^1J_{\text{Pt-P}}$ values for the triphosphine decrease as the $^1J_{\text{Pt-P}}$ values for the monophosphine increase. As a consequence of the rehybridization, we may also expect to observe different Pt–P bond distances to the triphosphine and monophosphine ligands of these complexes.

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(2) The mixed phosphine complexes Pt(triphosphine)PR$_3$ were prepared by either of two methods. Generally, the Pt(II) complex [Pt(triphosphine)(PR$_3$)Cl]Cl was prepared in situ by mixing an ethanol solution of PR$_3$ with a slurry of Pt(triphos)Cl$_2$ in ethanol. After stirring the mixture for 1 hr, an equal volume of water was added; then an aqueous solution containing 3 mol of NaBH$_4$ per mole of platinum was added over a period of 1 hr. Reduction is rapid, vigorous evolution of H$_2$ occurs, and the bright yellow Pt(0) complexes precipitate almost immediately from the aqueous ethanol. The second preparative method involved displacement of the PR$_3$ ligand by a more electronegative substituted monodentate phosphine in solution (e.g., benzene, toluene, or THF). The bis(diphosphine) cation $[Pt(Ph_2PCH_2CH_2CH_2PPh_2)_2]^{2+}$ was reduced similarly with NaBH$_4$ to give tetrahedral Pt(biphosphine)$_2$. All of the complexes described have satisfactory elemental analyses and proton and ^{31}P NMR spectra, and their preparations and properties will be presented in detail elsewhere. The Pt(triphosphine)PR$_3$ complexes are much more dissociatively stable than tetrakisarylphosphine complexes such as Pt(PPh$_3$)$_4$. For example, Pt(triphos)PPh$_3$ can be heated up to 60° in benzene before exchange of PPh$_3$ occurs, as indicated by ^{31}P NMR.

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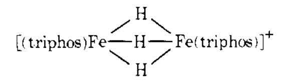
(8) The structures of three complexes of $CH_3C(CH_2PPh_2)_3$ have been determined and the P–M–P angles are fairly constant; e.g., mean P–M–P angles in Ni(triphos)C$_2$F$_4$,



$[(\text{triphos})\text{Fe}\overset{\text{H}}{\underset{\text{H}}{-\text{H}-}}\text{Fe}(\text{triphos})]^+$

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Nuclear Magnetic Resonance Studies on Effects of Ions (Anions and Cations) to Nucleosides (Cytidine and Guanosine)

Sir:

Metal ions in biological systems play a very important role, for example, the reaction between the enzyme and the substrate,[1] energy yielding metabolic processes,[2,3] and the highly ordered structure of nucleic acids.[4] Metal complexes of nucleosides may serve as a model, at least, for the interaction between nucleic acid and metal ion. In order to decide whether the group 2A metal ions have different biochemical natures from the group 2B with respect to complex formation with nucleosides, we have carried out proton resonance studies in the effect of the metal cations on the chemical shifts of the nucleosides.[5-7] Recently Chang et al.[8] reported that the chloride counterion binds to guanosine instead of the metal ions. However, coordination of the anion, such as Cl$^-$, to the nucleosides fails to explain the difference between the groups 2A and 2B in the effect to the chemical shifts.[7] In order to clear this discrepancy, we have carried out ^{1}H NMR and ^{13}C NMR studies on the interactions between the nucleosides (cytidine and guanosine) and salts of various combination of the divalent metal ions and the anions in DMSO solution. Our results indicate that both the metal ions and the anions influenced the chemical shift of ^{1}H NMR and ^{13}C NMR.

In a previous paper[6] we reported the interaction of divalent metallic chloride salts with cytidine in dimethyl sulfoxide. The most striking results we observed were that the [Mg^{2+}, Ca^{2+}] and [Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}] showed different effects regarding the chemical shift for the amino protons and also that in all the cases of the 2A and the 2B