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

Complex	$^1J_{Pt-P}$, Hz[a,b]	$^2J_{P-P}$, Hz[b]	$^1J_{Pt-P}$, 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_2Me	3075	51	5370
Pt(triphos)$P(OCH_2)_3CCH_3$	2990	68	6787
Pt(triphos)PF_2NMe_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 $^1J_{P-F}$, $^2J_{Pt-F}$, $^3J_{P-F}$ couplings are 1111.3, 639.7, and 43.0 ± 1 Hz, respectively. [g] The $^1J_{P-F}$, $^2J_{Pt-F}$, $^3J_{P-F}$ 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 $^1J_{Pt-P}$ is obtained from the linear plot of $^1J_{Pt-P(triphos)}$ vs. $^1J_{Pt-P(mono)}$ for the other monophosphine ligands.

the temperature range −50 to +60°) as a comparison standard with $^1J_{Pt-P}$ = 3644 ± 2.4 Hz, the $^1J_{Pt-P}$ values for the triphosphine are significantly smaller, whereas the $^1J_{Pt-P}$ values for the monodentate phosphines are much larger. Since the magnitude of the directly bonded coupling constant $^1J_{Pt-P}$ is dominated by the Fermi contact term,[1] changes in the magnitude of $^1J_{Pt-P}$ with phosphine within a series of platinum–phosphine complexes are largely dependent[7] on changes in $|S_P(0)|^2$ 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 $^1J_{Pt-P}$ values in Table I provide support for such a rehybridization and redistribution of s character, since the $^1J_{Pt-P}$ values for the triphosphine decrease as the $^1J_{Pt-P}$ 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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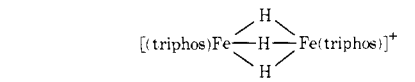
(7) $|S_P(0)|^2$ is the square of the magnitude of the s orbital of phosphorus evaluated at its nucleus and α_P^2 is the s character of the phosphorus lone pair orbital.

(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_2F_4,



and Ni(triphos)I are 92.5,[9] 89,[10] and 95.0,[11] respectively.

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(12) Address correspondence to this author at Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

Joseph Chatt, Ronald Mason, Devon W. Meek*[12]

School of Molecular Sciences, University of Sussex Brighton, England, BN1 9QJ

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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 ^1H 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 ^1H 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

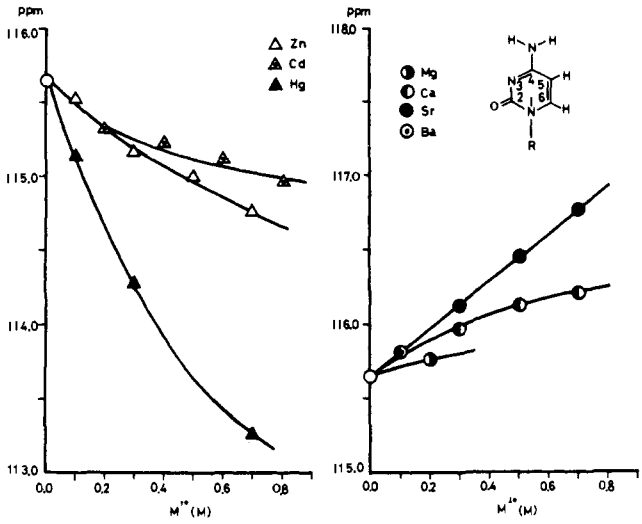

Figure 1. Depe idence of chemical shifts on the carbon 2 position of cytidine on the concentration of the group 2A and 2B metallic chlorides in DMSO at room temperature. (The chemical shift from DMSO.)

metal ions the peak attributed to the $4NH_2$ group in cytidine was found to be split into two peaks, which indicate nonequivalence of the amino protons due to hindrance of the rotation of the amino group.

Li et al.[9-11] reported that Zn^{2+} and Hg^{2+} are bound to the nitrogen atom at position 3 (3N). In the present work, we examine the interaction of both the cation and the anion with the nucleosides by ^1H NMR and ^{13}C NMR spectroscopy.

At first, we checked the effect of the anions, Cl^-, Br^- and I^-, to the chemical shifts of ^1H NMR. It was found that these anions with the fixed cation produced a large change in the limiting shift $\Delta\nu_{obsd}$ in the chemical shift of the amino proton and also a little change in the proton at the position 5 (5H) but no change in the proton at the position 6 (6H). The results of the amino proton shift induced by the addition of the salts of chloride, bromide, and iodide are given in Table I. The limiting shift of the amino proton is largest for Cl^- and smallest for I^-, namely in the order of Cl^-, Br^-, and I^-. It is worthy to note that the order of this increase in the chemical shift is the same as the order of decrease in the anion radius and quantitatively there is a linear relation between the ^1H NMR chemical shift of the amino proton and the reciprocal of the anion radius (r^{-1}). Furthermore, the concentration dependence of the line width was investigated. The signal attributed to the NH_2 line was broadened with increased concentration of CdI_2. On the other hand, addition of $CdCl_2$ produced no broadening. The above mentioned facts indicate that the anion interacts mainly with the amino proton in cytidine. Since both the cations and the anions have an effect on the chemical shifts of cytidine, the observed limiting shift $\Delta\nu_{obsd}$ should be considered the superposition of the effects of the two ions, namely

$$\Delta\nu_{obsd} = \Delta\nu_{cation} + \Delta\nu_{anion}$$

where $\Delta\nu_{obsd}$ is the observed limiting shift and $\Delta\nu_{cation}$ and $\Delta\nu_{anion}$ are the chemical shifts due to the cation and anion interacting with cytidine, respectively.

It is known that the ^{13}C chemical shifts of the heteroaromatic ring carbon are related to the electronic structure of the carbons.[12-15] The effects of the interaction of the chloride salts of the metal ions of group 2A (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) and 2B (Zn^{2+}, Cd^{2+}, Hg^{2+}) with cytidine in DMSO were observed by ^{13}C NMR spectroscopy. Addition of the salts leads to striking deviations in the chemical shifts in

Table I. The Values of the Limiting Shift ($\Delta\nu$ in Hz at 90 MHz) of Amino Protons in the Cytidine Complex

Cation	Chloride	Bromide	Iodide
Ca	86.7	73.8	35.9
Sr	152.6	72.7	
Zn	97.1	64.6	41.4
Cd	77.5	76.3	71.8

carbons 2 and 4 positions (2C and 4C) in cytidine. The signals of 2C were shifted downfield by adding 2A metal salts. On the other hand, the addition of the 2B metal salts caused the high field shift on the same carbon (Figure 1). This fact suggests that the metal ions of the 2A group (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) produced different effect from those by the 2B group (Zn^{2+}, Cd^{2+}, Hg^{2+}) with respect to the complex formation of cytidine. Moreover, among the 2A family the 4C is shifted to high field by the Mg^{2+} ion, whereas with the resonance peak nearly unaffected by Ca^{2+} and by addition of Sr^{2+} and Ba^{2+} the signal shifted to low field. Thus, one may consider that there are different subgroups in the 2A family concerning the effect of metal binding to cytidine.

Since the chemical shift is affected by both the cation and the anion, we must reconsider the estimation of the formation constants derived in previous papers.[6,10] We may presume that there are two formation constants in cytidine complex

$$Cl^- + Cyt \overset{k^-}{\rightleftharpoons} ClCyt^-$$

$$Ca^{2+} + Cyt \overset{k^+}{\rightleftharpoons} CaCyt^{2+}$$

If one can separately observe the $\Delta\nu_{anion}$ and $\Delta\nu_{cation}$ values, the constants k^- and k^+, can be determined from the observed limiting shift by the help of the equation given by Li et al.[9] It was found that in the cytidine complex the limiting shift of the proton at position 6 (6H) was independent of the species of the anions with the fixed cation. This fact seems to suggest that the limiting shift of 6H is determined merely by the cation, and the observed limiting shifts may be used for determining the formation constant k^+. In this way the formation constants of 1:1 cytidine metal ion complexes are obtained as follows: $MgCl_2$, 0.9 l./mol; $CaCl_2$, 3.5; $SrCl_2$, 4.5; $BaCl_2$, 11.7; $ZnCl_2$, 4.1; $CdCl_2$, 10.2; $HgCl_2$, 13.5. These obtained values of the k^+ indicate that the complexes of the cytidine with the cations are stable in the order of Ba, Sr, Ca, and Mg in the 2A group and Hg, Cd, and Zn in the group 2B.

The proton chemical shifts in the guanosine complex seem to be explained similarly to that of cytidine complex. Chang et al.[8] presented a model of the charge reversed chelate for an explanation for the observed change in the chemical shift of guanosine upon addition of the metal salts and concluded that not the metal ion but the chloride counterion is responsible either totally or substantially for the variation in the chemical shifts. However, the model of the charge reversed chelate compound fails to explain the following phenomena. (1) Different effects upon chemical shifts of guanosine are induced depending upon either the group 2A cation or 2B.[7] (2) Relatively small shifts were observed for the NH_2 and the NH resonance in $[NEt_4]Br$, NaBr, KBr, and $[NEt_4]I$. (3) Our present results are shown in Table II. The relative shift data for chloride, bromide, and iodide salts indicated that for various cations with fixed anion the ratio between the limiting shifts of the NH_2 and NH group was not constant. Moreover, the ratio is not constant with the different anions and the fixed cation.

Thus, even in the case of guanosine, these observed facts lead us to the conclusion that the phenomena are obviously very complex and both anion and cation may interact with

Table II. Ratio of Shifts of the NH_2 to NH Proton Resonance of Guanosine (0.1 *M*) in DMSO

Cation	Chloride	Bromide	Iodide
Li	1.05[a]	3.1[a]	
Na	1.05[a]	~3[a]	
K	~1[a]	~3[a]	
Mg	0.93[b]		
Ca	1.02[b]	2.44	~8.8
Sr	0.99[b]	1.27	
Ba	1.09[b]	~3[a]	
Zn	0.65[b]	0.23	0.33
Cd	0.16	0.19	0.17
Hg	0.61[b]		
Et_4N	1.09[a]		~4
Bu_4N		2.9[a]	

[a] From ref 8. [b] From ref 7.

guanosine and contribute to the complex formation of guanosine with both anion and cation. In general, one must consider that both the cations and the anions affect the interaction between the metal salts and the nucleosides in a complicated way.

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Tetsuro Yokono, Shigezo Shimokawa, Junkichi Sohma
Faculty of Engineering, Hokkaido University
Sapporo 060, Japan

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Stabilization of Cyclopropenium Ion by Nonbenzenoid Aromatics. Triferrocenylcyclopropenium Ion and Diferrocenylcyclopropenone

Sir:

Recent interest in cyclopropenium ion chemistry has focused on the stabilization of the "aromatic" but highly strained $2\pi 3C$ ring system by appropriate electron-donating substitutents, particularly heteroatoms.[1-3] In a search for alternative substituents which are capable of delocalizing the positive charge of the three-membered ring, we have considered the ferrocenyl group. The rationale underlying this approach was inherent in the unusual stabilization of carbenium ions adjacent to metallocenes.[4,5] We report straightforward syntheses and various properties of cyclopropenium ion and cyclopropenone *totally* substituted by ferrocenyl groups: triferrocenylcyclopropenium perchlorate (**1**) and diferrocenylcyclopropenone (**2**). We note the remarkable collective effect of the three ferrocenyl groups in stabilizing the C_3^+ ring in **1**. Ferrocenyldiphenylcyclopropenium tetrafluoroborate has previously been described, including its crystal and molecular structure.[6,7]

The synthetic route of choice was the electrophilic substitution of aromatic substrates by trichlorocyclopropenium salts (method of West and Tobey),[8-10] applied in dichloromethane. Treatment of $C_3Cl_3^+AlCl_4^-$ with ferrocene (2 mol equiv) in CH_2Cl_2 (5 hr at −70 to −80° and 30 min at 20°) gave a dark red complex which was decomposed (−60°) with aqueous acetone (20%). Purification by dry column chromatography (silica gel, ethyl acetate, R_f = 0.25) and recrystallization (benzene–petroleum ether 40–60°) afforded **2** as dark red crystals, mp 181° dec (yield, 7%; yield prior to recrystallization, 18%). Elemental analysis and spectral properties were all consistent with the formulation of **2**. The mass spectrum revealed the fragmentation $M\cdot^+$ (*m/e* 422, 6%) → $[M - CO]\cdot^+$ (*m/e* 394, 100%) (substantiated by appropriate metastable transitions). Ir, ν_{max} (KBr) 3095 (w), 2920 (w), 1850 (vs), 1820 (m), 1612 (vs), 1475 (s), 1105 (s), 892 (m), 839 (s), 815 (s), 727 (m), 514 (m), 496 (s), and 482 (s) cm^{-1}. Noteworthy are the infrared bands at 1850, 1820, and 1612 cm^{-1} which are diagnostic for the cyclopropenone nucleus.[10-12] Uv, λ_{max} (EtOH) 243 (log ϵ 4.15), 275 (4.08), 300 (4.08), 348 (3.71), and 477 nm (3.33). NMR:[13] δ ($CDCl_3$) 4.23 (10 H, s, 1′-H), 4.56 (4 H, t, J = 2 Hz, β − H), and 4.83 (4 H, t, J = 2 Hz, α − H); δ (C_6D_6) 3.94 (10 H, s), 4.13 (4 H, s, broad), and 4.60 (4 H, s, broad). δ (α − H), $\delta(\beta$ − H), $\Delta\delta(\delta(\alpha$ − H) − $\delta(\beta$ − H)), the benzene induced solvent shifts, and the pattern of the NMR spectra closely resemble those of ferrocenecarboxaldehyde.[14] The shift of $\delta(\alpha$ − H) to lower field is due mainly to the anisotropy of the cyclopropenone system, including the diamagnetic anisotropy of the carbonyl group. The electric dipole moment of **2**, 5.37 D (benzene, 30°, α' = 41.60, β' = 3.09, MR_{calcd} = 109.56 cm^3, $P_{2\infty}$ = 689.4 cm^3) was only slightly higher than the corresponding moment of diphenylcyclopropenone[10] (5.08 D). A substantial displacement of the (modest) positive charge from the three-membered ring into the ferrocenyl moieties was not observed.

The analogous reaction of $C_3Cl_3^+AlCl_4^-$ with 3 mol equiv of ferrocene in CH_2Cl_2 (3 hr at −70°, 16 hr at 23°, 2 hr reflux, decomposition at −60° by aqueous acetone (20%)) followed by treatment with perchloric acid (70%) led to **1**. Purification by dry column chromatography (microcrystalline cellulose, CH_2Cl_2–petroleum ether 40–60°) and recrystallization (CH_2Cl_2–petroleum ether 40–60°) gave **1** as dark red crystals, mp 171° dec (explosive) (yield, 38%).[15] Uv, λ_{max} (CH_2Cl_2) 309 (log ϵ 4.42), 363 (3.98), and 520 nm (3.85). Ir, ν_{max} (KBr) 3120 (w), 2930 (w), 1860 (w), 1494 (vs), 1412 (m), 1384 (s), 1359 (m), 1146 (m), 1120 (s), 1100 (vs), 1052 (m), 1030 (m), 1000 (m), 900 (m), 820 (m), 675 (w), 620 (m), 490 (s), and 478 cm^{-1} (s). The very strong infrared band at 1494 cm^{-1} is indicative of the cyclopropenium ion;[1,12,16] it is assigned to the unsymmetric degenerate stretching vibration (E′) of the C_3^+ ring.[1,16] The cyclopropenium structure of **1** was strikingly verified by the characteristic Raman absorption at 1860 cm^{-1} due to the totally symmetric stretching vibration (A_1') of the aromatic C_3^+ ring.[1,12,16] NMR:[13] δ ($CDCl_3$) 4.38 (15 H, s, 1′ − H), and 5.13 (12 H, s, broad, α − H, β − H); δ (CD_3CN) 4.35 (15 H, s, 1′ − H), 5.08 (6 H, s, broad, β − H or α − H), and 5.17 (6 H, s, broad, α − H or β − H). The collapse of $\Delta\delta$ (**1**) may reflect two opposing effects: as a ferrocenylcarbenium ion, $\Delta\delta$ should be negative,[5] while as a substituted cyclopropenium ion, $\Delta\delta$ should be positive.

Finally, the "aromatic" stabilization of **1** may be inferred from its high pK_{R+}, >10 (potentiometric titration method,[17,18] 50% aqueous CH_3CN). The corresponding pK_{R+} values of triphenyl- and the triaminocyclopropenium ions are 3.1,[17] and >10,[1,16,18] respectively. These results clearly