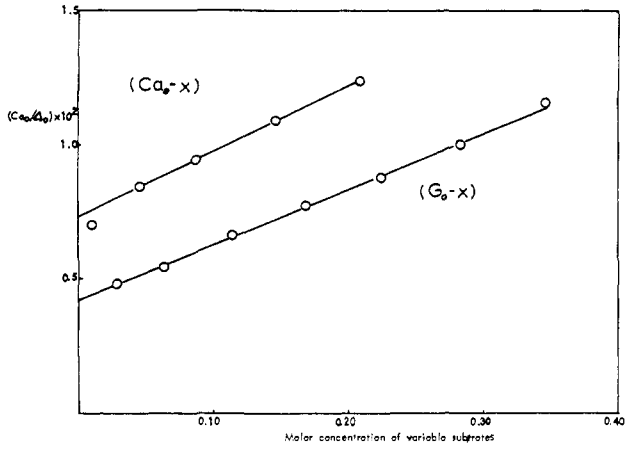


Figure 1. Plot used in determining K.

Table I. Chemical Shifts of Guanosine–Calcium(II) Complex[a]

$[CaCl_2]$,[d] M	[Guanosine],[b] M	ν_G(N(2)–H$_2$),[c] Hz	ν_0(N(2)–H$_2$), Hz	Δ_0
0.0			389	0
0.084			401	12
0.168			409	20
0.253			416	27
0.338			420	31
0.422			423	34
	0.070	385	414	29
	0.141	387	413	26
	0.211	389	410	21
	0.282	389	407	18
	0.352	390	406	16
	0.423	392	406	14
	0.493	393	405	12

[a] Measured at 37°, 60 MHz on Varian A-60, chemical shifts with respect to TMS, terms defined in text. [b] [G] = 0.282 M, for varying $CaCl_2$. [c] ν_G(N(2)–H) = 389 Hz. [d] $[CaCl_2]$ = 0.141 M for varying guanosine.

Preliminary data at 122° give a K of 10 ± 2. (2) The complex is shown not to be an artifact of the solvent DMSO alone since addition of $CDCl_3$ does not destroy it. (3) The complex has also been found to exist in partially aqueous solution. Following the procedure of Yates and Welch[4] we titrated guanosine and guanosine + $CaCl_2$ (1:4 molar ratio) at 25° in 70% by wt DMSO–H_2O (1:2 mole ratio) with a glass electrode (Radiometer pHm 26). The pK_a for loss of N(1)–H is 11.25 without and 9.6 with the $CaCl_2$ present in this mixture,[5] implying that the presence of Ca^{2+} enhances acidity. A titration in pure H_2O gave very small changes for a 1:1 molar ratio (near 0.1 pK lowering by Ca^{2+}) in the same direction as was found in a DMSO–H_2O mixture. (4) The resonances attributed to N(1)–H and N(2)–H show marked broadening upon Ca^{2+} addition implying an intermediate exchange rate for the process. The observed peak areas are apparently unaffected by the exchange process within nmr integration limits. (5) The C(8)–H resonance shows sharpening upon complexation perhaps due to enhanced lactim–lactam tautomerization as suggested recently.[6]

(4) K. Yates and G. Welch, *Can. J. Chem.*, 50, 474 (1972).
(5) The 2-pK unit shift of guanosine from the value in aqueous solution is similar to the shifts observed in ref 4.
(6) G. C. Y. Lee and S. I. Chan, *J. Amer. Chem. Soc.*, 94, 3218 (1972).

We do not have any immediate suggestions concerning the biochemical significance of such a highly specific complex between the pyrimidine ring of guanosine and Ca^{2+}. One may note the Ca^{2+}-mediated cyclic GMP effect on cyclic AMP function,[7] however, as well as the known binding of Ca^{2+} by RNA.[8]

We are continuing the characterization of the complex along the evidence here outlined and plan eventual X-ray determination of the structure to unequivocally establish the mode of Ca^{2+} binding.

Acknowledgment. A research grant from the Rutgers University Research Council supporting this work is gratefully acknowledged.

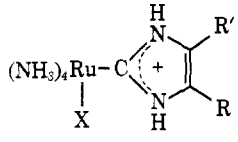
(7) J. F. Whitfield and J. P. MacManus, *Proc. Soc. Exp. Biol. Med.*, 139, 818 (1972).
(8) H. S. Loring and R. S. Waritz, *Science*, 125, 644 (1957).

Frank Jordan,* B. Y. McFarquhar
Department of Chemistry, Rutgers University
Newark, New Jersey 07102
Received July 10, 1972

Carbon-Bound Imidazolium Ylides as Ligands in Ruthenium(II) and Ruthenium(III) Complexes

Sir:

Investigation of the acid-catalyzed aquation of the ion $[(NH_3)_5Ru(II)Im]^{2+}$ [1,2] has shown that the rate is pH and ionic-strength dependent qualitatively like the hydrolysis of $[(NH_3)_5Ru(II)py]^{2+}$,[3] although the rate is some 500 times greater for the imidazole complex. The major product of acidic cleavage is $[(NH_3)_5Ru(II)H_2O]^{2+}$ isolated as $[(NH_3)_5Ru(III)Cl]Cl_2$ after oxidation. There is also formed an imidazole-containing species isolated (<10%) after air oxidation as a solid having the composition $(NH_3)_4Ru(III)ImCl_3$. We consider the imidazole in both the Ru(II) and Ru(III) states of this ion to be bound *via* C-2 of the imidazole ring as shown for **1a**. The proton nmr spec-



1a, R = R′ = H
b, R = R′ = CH_3
c, R, R′ = benzo
d, R = H; R′ = CH_3

trum of the Ru(II) species in D_2O or H_2O displays a single line for carbon-bound protons at 7.2 ppm.[4] The ammine protons appear as a broad signal at 1.9 ppm.

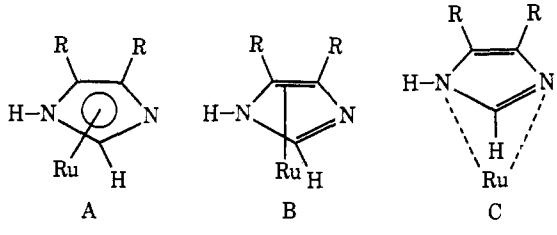
(1) Abbreviations: Im = imidazole; MIm = 4-methylimidazole, DMI = 4,5-dimethylimidazole; BZI = benzimidazole.
(2) This ion, characterized as the BF_4^- salt, was prepared by the procedure of R. G. Gaunder and H. Taube, *Inorg. Chem.*, 9, 2627 (1970). Proton nmr data show that it is a typical imidazole complex bound through the "pyridine nitrogen." Three C–H signals are observed at δ 7.04, 7.29, and 7.75 in D_2O. The uv spectrum consists of a band at 255 nm (ε 2800) with a prominent shoulder at 280 nm (ε 2700). Air oxidation gives the Ru(III) species isolated as the trichloride: λmax 300 nm (ε 1880), 430 (250).
(3) P. C. Ford, J. R. Kuempel, and H. Taube, *ibid.*, 7, 1976 (1968); R. E. Shepherd, Ph.D. Thesis, Stanford University, 1971.
(4) Chemical shifts are relative to sodium 3-trimethylsilylpropionate-2,2,3,3-d_4.

The signal at 7.2 ppm is assigned to the equivalent protons on C-4 and C-5 and the absence of other signals is consistent with the carbon-bound structure.

A 4,5-dimethyl analog **1b** can be prepared directly from $[(NH_3)_5Ru(II)H_2O)]^{2+}$ and a DMI–DMIH$^+$ buffer system at pH 5.5. Air oxidation followed by isolation by ion-exchange chromatography gives a purple solid of composition $(NH_3)_4Ru(III)DMICl_3$. The nmr spectrum of the Ru(II) species consists of two lines, a sharp singlet at 2.1 ppm assigned to the chemically equivalent methyl groups and a broader peak at 1.9 ppm assigned to the ammine groups. No signal attributable to a proton bound to C-2 could be found in the region ±1000 Hz from water. The ^{13}C nmr spectrum measured in D_2O by the pulse Fourier transform technique shows signals at 13.4 and 128 ppm downfield of TMS. We were unable to observe a signal attributable to the metal-bound carbon in the region 0–600 ppm.[5] Although the limited amount of data on ^{13}C spectra of complex ions prevents a precise prediction of the position of the resonance for C-2 in structure **1b**, an extreme downfield position is to be expected on the basis of previous observations.[6]

Benzimidazole forms primarily a nitrogen-bonded complex $[(NH_3)_5Ru(II)BZI]^{2+}$[7] on reaction with $[(NH_3)_5Ru(II)H_2O]^{2+}$, but acid treatment gives a low yield of the carbon-bound species **1c** which has an nmr spectrum with aromatic multiplets of the AA′BB′ type characteristic of a symmetrically ortho-disubstituted benzene centered at 7.14 and 7.34 ppm. No peak assignable to a C-2 proton was observed. The Ru(III) complex was isolated as a crystalline solid and had the composition $(NH_3)_4RuBZICl_3$. 4-Methylimidazole also reacts directly with $[(NH_3)_5Ru(II)(H_2O)]^{2+}$ to give primarily the N-bound species,[7] but after treatment with acid and air oxidation **1d** is obtained as the trichloride.

The nmr results demand that **1a**, **1b**, and **1c** have a symmetrical disposition of the ligand relative to the ruthenium. None of the alternatives to structure **1** we have conceived of can be reconciled with the available data. π-Bonded structures such as A, B, and C,



rendered symmetric by rapid exchange of a proton between the N atoms, would not explain the absence of a signal for the 2 proton.

The formal ligand in these ions is the imidazolium ylide, a neutral dipolar molecule, not previously recognized as a ligand in transition metal complexes. Its role in deuterium exchange processes and other reactions of imidazole derivatives has, however, been established.[8] The related 1,3-dimethylimidazolium ylide has been characterized in a tetracarbonyliron(0) complex.[9] The nature of the carbon atom involved in metal bonding also has some similarities to those found in the various "carbene" metal complexes of Fe(II), Pd(II), and Pt(II) bearing alkoxy and amino substituents.[10] The fact that each of the solid Ru(III) species has been characterized as **a** tetraammine by elemental composition implies a strong labilizing effect of the carbon-bound ligand on one coordination site, presumably trans. This implication and stereochemical assignment remain to be studied in detail, however. Conductivity data in water on the trichloride salt of ion **1b** indicate it to be a 1:3 electrolyte. Ion-exchange elution behavior is also suggestive of a +3 charge. Thus, while there may be a coordinated chloride in the anhydrous solid, it must be substantially dissociated in aqueous solution.

The Ru(III) complexes show solvent-sensitive charge-transfer bands in the visible as follows: **1a**, 480 nm (ε 1630); **1d**, 545 (2860); **1b**, 600 (4700). The Ru(II) species are colorless but absorb strongly near 260–265 nm.

The potential significance of these observations to considerations of structure and function of metallo enzymes and hemoproteins, in particular, should be noted. To the extent that the low-spin Ru(II) and Ru(III) systems studied are appropriate models for low spin Fe(II) and Fe(III), in heme environments, for example, our results imply that histidine residues could adopt either the conventional nitrogen-bonded orientation, which would presumably be strongly favored in high-spin Fe(II), or a carbon-bound structure of the type reported here. It is conceivable that the alternative bonding mode could function to effect trans ligand lability, to couple protein conformation with oxidation potential, or the adoption of the alternative bonding mode could serve to trigger a general conformational change in the protein.

Acknowledgment. Support of this research by NIH Grant GM 13638-07 and NSF Grant GP 24726X is gratefully acknowledged. Some of the nmr spectra were carried out on a Varian XL-100 instrument purchased with support of NSF Grant GP 28142.

(5) Spectra were recorded on 0.1 *M* solutions in D_2O. Some samples were also 4×10^{-3} *M* in Mn(II). The reported peaks were easily observed in spectra from 20,000 transients. Sample stability limits the observation to about 60,000 transients.

(6) C. G. Kreiter and V. Formacek, *Angew. Chem., Int. Ed. Engl.*, **11**, 141 (1972); L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971); O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, **94**, 2550 (1972).

(7) The nitrogen-bound complexes $[(NH_3)_5RuBZI]^{2+}$ and $[(NH_3)_5RuMIm]^{2+}$ are oxidized by air to the corresponding Ru(III) species which have been isolated as trichlorides.

(8) R. A. Olofson, W. R. Thompson, and J. S. Michelman, *J. Amer. Chem. Soc.*, **86**, 1865 (1964); T. M. Harris and J. C. Randall, *Chem. Ind. (London)*, 1728 (1965); P. Haake, L. P. Bausher, and J. P. McNeal, *J. Amer. Chem. Soc.*, **93**, 7045 (1971).

(9) K. Öfele, *Angew. Chem., Int. Ed. Engl.*, **8**, 916 (1969); K. Öfele and C. G. Kreiter, *Chem. Ber.*, **105**, 529 (1972).

(10) E. M. Badley, J. Chatt, and R. L. Richards, *J. Chem. Soc. A*, 21 (1971); F. Bonati and G. Minghetti, *J. Organometal. Chem.*, **24**, 251 (1970); F. Bonati, G. Minghetti, T. Boschi, and B. Crociani, *ibid.*, **25**, 255 (1970); R. J. Angelici and L. M. Charley, *ibid.*, **24**, 205 (1970); J. Miller, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, **93**, 4613 (1971); B. Crociani, T. Boschi, and U. Belluco, *Inorg. Chem.*, **9**, 2021 (1970); H. C. Clark and L. E. Manzer, *ibid.*, **11**, 503 (1972).

(11) National Institutes of Health Special Research Fellow on leave from the University of Virginia, Charlottesville, Va.

Richard J. Sundberg,*[11] Rex E Shepherd, Henry Taube*

Department of Chemistry, Stanford University
Stanford, California 94305

Received June 12, 1972