Additivity of Carbon-13 Chemical Shifts in 2,2'-Bipyrimidine Monometallic and Bimetallic Complexes of Tetraammineruthenium(II)

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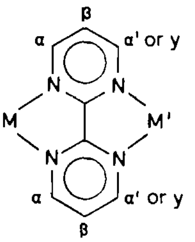
There have been previous reports describing the coordination of aromatic, nitrogen heterocyclic ligands to transition metal centers such as $Fe(CN)_5^{3-}$ [1, 2] or $Ru(NH_3)_5^{2+}$ [3] and its effect on the ^{13}C NMR chemical shifts of the ligand. The bonding between the d^6 low spin metal center and the ligand can be described as σ-donation from the ligand to the metal in conjunction with π-backdonation from the metal to the ligand [4]. For both ^{13}C and ^1H NMR spectra of azines bound to $Fe(CN)_5^{3-}$ [1, 2], the α-C and α-H chemical shift moves downfield with respect to that of free ligand while the β-C, β-H, γ-C and γ-H all shift upfield from free ligand values. The shielding of the β- and γ-nuclei upon coordination has been ascribed to the π-backdonation into the azine ring from the π-symmetry, filled orbitals on Fe [1, 2]. The deshielding of the α-C and α-H resonances upon coordination are harder to interpret. This type of shift occurs for pyridine and pyrazine complexes of $Fe(CN)_5^{3-}$ [1, 2], $Co(CN)_5^{2-}$ [1], $Co(NH_3)_5^{3+}$ [3], $Rh(NH_3)_5^{3+}$ [3], and $Ru(NH_3)_5^{2+}$ [3]. This effect cannot be due just to cyano ligand, and all of the other terms such as $N-C_\alpha$ bond polarization [5], temperature-independent paramagnetism due to the metal [3], remote (metal-centered), anisotropic, diamagnetic currents, and increased electron density due to π-backbonding [1–3] should have net shielding contributions at α-carbon.

One of the questions we wished to answer with this study was the nature of the α-carbon deshielding in $Fe(CN)_5L^{3-}$ and $Ru(NH_3)_5L^{2+}$ complexes. Since the L ligand is planar (*i.e.*, γ-substituted pyridine or pyrazine), the symmetry of the complexes (neglecting H atoms of NH_3) are C_{2v}. We have prepared [6] the compound tetraammine-2,2'-bipyrimidineruthenium(II), $Ru(NH_3)_4(bpym)^{2+}$, which also has C_{2v} symmetry and the same type of metal-azine bonding. In this complex the α-carbon of bpym does not lie near the shielding cone as it does for $Ru(NH_3)_5L^{2+}$.

TABLE I. Carbon-13 NMR Spectra of Free and Bound 2,2'-Bipyrimidine.[a]



M	M'	α	δ (^{13}C), ppm[b]	
			β	α' or γ
		159.1	123.4	159.1
$Ru(NH_3)_4^{2+}$		162.0	123.3	154.4
		(+2.9)	(−0.1)	(−4.7)
$Ru(NH_3)_4^{2+}$	$Ru(NH_3)_4^{2+}$	157.2	123.0	157.2
		(−1.9)	(−0.4)	(−1.9)
expected-experimental		−0.1	+0.2	−0.1

[a] Proton-decoupled ^{13}C spectra recorded on a JEOL FX90Q spectrometer operating a 22.5 MHz. [b] Chemical shift, reported *vs.* external TMS in D_2O (dioxane as int. ref.) in 0.1 *M* solutions of complex.

If through-space interactions (*i.e.*, TIP or remote, anisotropic, diamagnetic currents) are causing the α-carbon shifts, differences should be observed for $Ru(NH_3)_5py^{2+}$ and $Ru(NH_3)_4(bpym)^{2+}$. However, as Table I indicates, the same pattern is observed for $Ru(NH_3)_4(bpym)^{2+}$ as the monodentate L system, deshielding at α-carbon and shielding at β- and γ-carbons. Although the actual source of the shift is not at this time understood, these data strongly suggest that the deshielding at α-carbon is due to a through-bond interaction such as $N-C_\alpha$ bond polarization, or changes in the electron density *via* σ-donating/π-accepting characteristics of the ligand [7].

A second point we wished to persue was the fact that some evidence exists for long range additivity of ^{13}C resonance in bimetallic systems through monodentate bridging ligands [1]. If, in fact, all contributors to the chemical shift are acting independently of each other, then a severe test of this hypothesis would be to bring the two metals very close together. We have prepared the bimetallic complex, $[Ru(NH_3)_4]_2(bpym)^{4+}$ [6] and the results of the proton-decoupled ^{13}C NMR spectrum appears in Table I as well. For this compound, all ^{13}C resonances appear upfield from free ligand. The last line in Table I, labeled as expected-experimental, indicates the

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degree of chemical shift additivity in going from the monometallic to bimetallic compound. The expected shift is obtained by applying α, β, and γ shifts (δ $(Ru(NH_3)_4(bpym)^{2+})$ – δ(bpym)) from the M′ to the spectrum of $Ru(NH_3)_4(bpym)^{2+}$, thus generating an expected spectrum. The difference between expected and experimental is quite small as indicated in Table I. Apparently, all contributors to the ^{13}C chemical shifts are acting independently and are not being influenced by a second metal center.

The only report of a d^6 metal system bound to an azine with different properties is the Group VI B carbonyl compounds, $M(CO)_4L$, where M = Mo, W and L = 2,2′-bipyridine or 2,2′-bipyrimidine [8]. In $CDCl_3$, all ^{13}C NMR resonances are downfield from free L. This may be a result of the non-aqueous solvent or a reduced amount of π-backbonding in the Group VI B carbonyls *vs.* the Ru(II) ammines or Fe(II) cyano compounds. Further studies in this area are currently underway [9].

Lastly, it should be noted that the magnitude of the upfield shift of the γ-C with respect to the free ligand has been interpreted as a measure of the amount of $d_\pi \rightarrow p_\pi^*$, π-backbonding [1–3]. The –4.7 ppm chemical shift in γ-C for $Ru(NH_3)_4(bpym)^{2+}$ is larger than any other γ-C shift reported for $Ru(NH_3)_5(py\text{-}X)^{2+}$ or $Fe(CN)_5(py\text{-}X)^{3-}$ complex. This result suggests a large amount of π-backbonding in $Ru(NH_3)_4(bpym)^{2+}$, which is consistent with the electrochemical studies on this system [6].

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