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Analysis of the ^{1}H and ^{13}C NMR Spectra of $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}$: Evidence for a Carbon-Bonded Structure

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Received September 16, 1982

The 500-MHz proton and 125-MHz carbon-13 NMR spectra of $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}$ in $Me_2SO\text{-}d_6$ indicate the presence in the complex of a unique bipyridine ligand bound to the Ir^{III} via the 3-carbon of one pyridine ring and the nitrogen of the other pyridine ring, in agreement with recent X-ray crystal structure data. Experiments using the lanthanide shift reagent $Pr(fod)_3$ confirm the presence of a site of Lewis basicity in the carbon-bonded pyridine ring. The sensitivity of resonances of this ring to temperature and solvent suggests that conformational changes may occur in the complex. Single-frequency off-resonance proton-decoupled ^{13}C NMR spectra indicate seven carbon resonances that have no strong C–H coupling, these arising from the six bridging 2- and 2′-carbons and the one 3-carbon bound to iridium.

Introduction

A previous study[1] of the ^{13}C NMR spectrum of the $[Ir(bpy)_2H_2O(bpy)]Cl_3$ complex ion, originally formulated as aqua(2,2′-bipyridine-*N*)bis(2,2′-bipyridine-*N,N′*)iridium(III) chloride, indicated a fully aromatic carbon spectrum for the solvated species in dimethyl-d_6 sulfoxide ($Me_2SO\text{-}d_6$). This excluded the possibility of formulation of its structure in terms of covalent hydration[2] and supported a monodentate bpy (2,2′-bipyridine) structure.[3,4] A recent X-ray crystal structure determination[5] indicated that the complex features an Ir–C bond in the solid state, consistent with full aromaticity of the pyridine rings and the presence of an uncoordinated N atom in a pyridine ring. While the X-ray data would not permit differentiation of a carbon from a nitrogen atom, the presence of one outer-sphere oxygen atom suggested to Serpone et al. that metalation had occurred at the 3-carbon of a pyridine ring to give a complex formulated as ((*N*H)-2,2′-bipyrid-3-ylium-C^3,*N′*)bis(2,2′-bipyridine-*N,N′*)iridium(III) perchlorate, $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2](ClO_4)_3$. In order to further elucidate the structure of the solvated complex ion, we have performed a series of measurements of the ^1H NMR spectrum, including homonuclear decoupling and lanthanide shift reagent effects, and of the ^{13}C NMR spectrum, including single-frequency off-resonance decoupling. We report the assignment of the 500-MHz ^1H NMR spectrum in $Me_2SO\text{-}d_6$ and the effect of the lanthanide shift reagent $Pr(fod)_3$, tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)praseodymium, on the ^1H NMR spectrum in acetonitrile-d_3 (ACN-d_3). Solvent and temperature effects on the ^1H NMR are also noted. In the ^{13}C spectra obtained at field strengths greater than that available earlier,[1] we can identify the resonance of the carbon bound to iridium. Both spectroscopies confirm the suitability of the formulation $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}$ to the complex in solution.

Experimental Section

Chemicals. Dimethyl-d_6 sulfoxide and acetonitrile-d_3 were obtained from Stohler Isotope Chemicals and were distilled from CaH_2 and stored over Baker and Adamson 4A molecular sieves. $Pr(fod)_3$ was obtained from Aldrich Chemical Co. $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}$ was prepared according to previously described procedures.[3]

Techniques. High-field NMR spectra (except the two-dimensional *J* spectrum) were obtained on the Bruker WM 500 instrument at the Southern California Regional NMR Facility. Chemical shifts and coupling constants in proton spectra were obtained from resolution-enhanced Fourier transforms of approximately 100 fid's. Chemical shifts were referenced in each case to solvent, except as noted. Selective homonuclear decoupling was utilized to facilitate assignment of resonances.

The two-dimensional homonuclear *J*-correlated proton spectrum was obtained on a Nicolet NT-300 spectrometer (300 MHz for protons), with use of a program supplied by Nicolet, COSY4.[6] Data were collected on samples of $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}$ in $Me_2SO\text{-}d_6$.

In studies of the effect of $Pr(fod)_3$ on the ^1H NMR of $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}$, the relative concentration of $Pr(fod)_3$ to $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}$ was varied from 0 to 9 in acetonitrile-d_3. Absorption spectra of the $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}\text{–}Pr(fod)_3$ solutions were monitored with a Cary 15 spectrophotometer.

^{13}C NMR spectra were measured with the Bruker WM 500 (125 MHz for ^{13}C), each spectrum made from approximately 10000 scans. Proton resonances were either broad-band decoupled ($^{13}C\{^1H\}$) or single-frequency off-resonance decoupled. The latter technique, which makes evident strong $^{13}C\text{–}^1H$ couplings, was used once with the irradiation frequency upfield and once with it downfield of the sample's proton resonances. A $^{13}C\{^1H\}$ spectrum was obtained on the Nicolet NT-300 (75 MHz for ^{13}C) for determination of the field dependence of carbon resonances.

Results and Discussion

Proton NMR. The aromatic region of the ^1H NMR spectrum of the title complex appears in Figure 1. Results of the decoupling experiments and the assignments of proton resonances based on these experiments are summarized in Table I. Discussion of these data is made with reference to six distinct pyridine rings, labeled as in Figure 2. The two distinct high-field multiplets (δ 6.70 and 7.16) are coupled to each other and to the resonance at δ 8.46. These three resonances are not coupled to any other resonances, and each of the three integrates to one proton in approximately twenty-three. Comparison with known[7] proton coupling constants in free bipyridine and in $[Fe(bpy)_3]Cl_2$ leads us to assign these three chemical shifts to protons A-4, A-5, and A-6. These and other assignments with coupling constants are also summarized in Table I. *It is most significant that coupling of A-4, A-5, and A-6 to A-3 is not observed nor is any resonance attributable to A-3 found.*

Each of the four protons in the B ring resonates in an open portion of the spectrum without overlap by other resonances, thereby facilitating assignment of the B-ring resonances. Coupling constants of the four protons in the B ring are consistent with previous data.[7]

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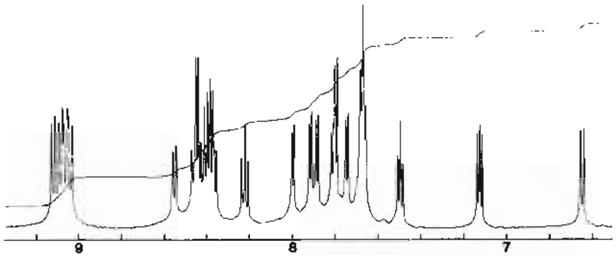

Figure 1. Aromatic region of the 500-MHz ^1H NMR spectrum of $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}$ in $Me_2SO\text{-}d_6$ at 22 °C. Resolution enhancement, used in assigning coupling constants, is not featured in this spectrum. Chemical shifts are in units of δ.

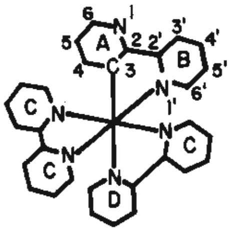

Figure 2. Carbon-bonded structure of $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}$. Reasons for labeling rings A and B are presented in text; three C rings and ring D are labeled as shown because it is thought the trans effect of carbon would differentiate the proton chemical shifts of one pyridine ring.

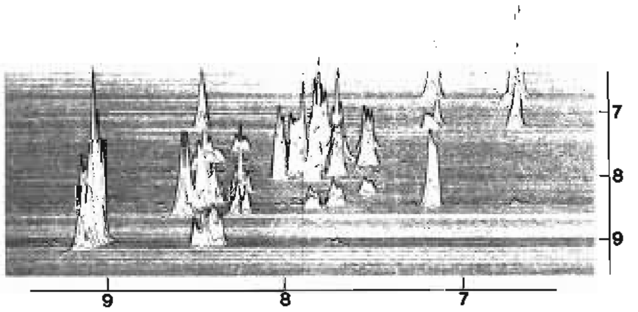

Figure 3. Two-dimensional homonuclear correlation spectrum of $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}$. The spectrum results from the double Fourier transformation of a 512 by 512 time-domain matrix.

The remaining resonances derive from four pyridine ring systems of four spins each. Three of the rings (C, C′, and C″) are very similar in the chemical shift of corresponding spins and cannot be distinguished from one another by decoupling. The four spins in the D-ring system are close to those of the C rings but can be distinguished from them by decoupling.

The 2D *J*-correlated spectrum (Figure 3) indicates a three-spin A ring. Most signals appear along a diagonal that runs from the left foreground to the right background. Peaks off this diagonal arise from the modulation of one proton signal at the frequencies of protons coupled to it. Multiplets at δ 6.7 and 7.2 are coupled to one another, to a multiplet at δ 8.5 and apparently to no other resonance. These data are consistent with the decoupling results.

Variation of the solvent from $Me_2SO\text{-}d_6$ to $ACN\text{-}d_3$ or D_2O was found to cause substantial changes in the spectral width as summarized in Table II. Chemical shifts of the three A-ring protons were found particularly sensitive to solvent and are included in Table II. Temperature dependence of the A-ring resonances was also noted.

Addition of the lanthanide shift reagent, $Pr(fod)_3$, to $ACN\text{-}d_3$ solutions of the complex resulted in a significant increase in the width of the aromatic region of the spectrum. As with solvent and temperature effects noted above, the resonances associated with the A-ring protons were most sensitive to the presence of $Pr(fod)_3$ in the solution (see Table

Table I. Assignment of ^1H NMR Spectrum of $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}$ in $Me_2SO\text{-}d_6$ at 30 °C

chem shift of multiplet, δ	obsd coupling, Hz	assign of coupling	assign of multiplet
6.70	7.6	$J_{4,5}$	A-4
	1.5	$J_{4,6}$	
7.16	7.5	$J_{4,5}$	A-5
	4.8	$J_{5,6}$	
8.46	4.8	$J_{5,6}$	A-6
	1.5	$J_{4,6}$	
7.50	7.5	$J_{4,5}$	B-5
	5.7	$J_{5,6}$	
	1.5	$J_{3,5}$	
7.76	5.7	$J_{5,6}$	B-6
	1.5	$J_{4,6}$	
	0.7	$J_{3,6}$	
8.24	7.7	$J_{4,3}$	B-4
	7.6	$J_{4,5}$	
	1.0	$J_{4,6}$	
8.62[a]	8.0	$J_{3,4}$	B-3
	1.7	$J_{3,5}$	
	0.7	$J_{3,6}$	
7.64–7.70	*b*	*b*	3 C-5
7.80	5.6	*c*	C-6
	1.0		
7.88, 7.93	5.6	$J_{5,6}$	2 C-6
	1.6	$J_{4,6}$	
	0.9	$J_{3,6}$	
8.36, 8.38, 8.41	7.5	$J_{4,3}$	3 C-4
	7.8	$J_{4,5}$	
	1.2	$J_{4,6}$	
9.04, 9.06, 9.08	8.4	$J_{3,4}$	3 C-3
	1.3	$J_{3,5}$	
	0.8	$J_{3,6}$	
7.81	5.5	*c*	D-5
	1.1		
7.99	5.6	$J_{5,6}$	D-6
	1.6	$J_{4,6}$	
	1.0	$J_{3,6}$	
8.45[d]	8.0	$J_{4,3}$	D-4
	8.0	$J_{4,5}$	
	1.5	$J_{4,6}$	
9.12	8.5	$J_{3,4}$	D-3
	1.3	$J_{3,5}$	
	1.3	$J_{3,6}$	

[a] Due to broadening of this resonance at 30 °C, coupling constants were obtained from spectrum of sample at 85 °C. [b] Complex multiplet appears centered at δ 7.68. Individual coupling constants cannot be determined. [c] Overlapping multiplets due to C-6 and D-5 prevent assignment of coupling constants. [d] Estimated from overlap with A-6 (δ 8.46) and decoupling at δ 6.7.

Table II. Solvent and Temperature Effects on ^1H NMR

solvent	temp, °C	chem shifts[a] of A ring			lowest field resonance, δ	width of aromatic region, ppm	notes
		A-6	A-5	A-4			
$Me_2SO\text{-}d_6$	30	8.46	7.16	6.70	9.12	2.46	
	22	8.44	7.12	6.64	9.12	2.52	*b*
	85	8.42	7.07	6.61	9.06	2.50	
D_2O	30	8.30	7.14	6.99	8.54	1.59	*c*
$ACN\text{-}d_3$	30	8.60	7.54	7.49	8.67	1.21	*d*
	30	8.45	7.21	6.93	8.66	1.76	*e*

[a] All values of chemical shift in δ, referenced to solvent, except as noted. [b] B spins also shift upfield, especially B-3 which shifts 0.07 ppm. [c] Chemical shift referenced to *t*-BuOH and dependent on concentration of complex. [d] No $[Pr(fod)_3]$ added. [e] With $[Pr(fod)_3]$ such that $[Pr^{3+}] = 3[Ir^{3+}]$. A-4 resonance is slightly broadened. B-5 and B-4 resonances shift upfield by about 0.14 ppm; B-6 and B-3, by smaller amounts. Chemical shifts of three C-6 spins change by about 0.10 ppm. Chemical shifts of other spins are essentially unchanged.

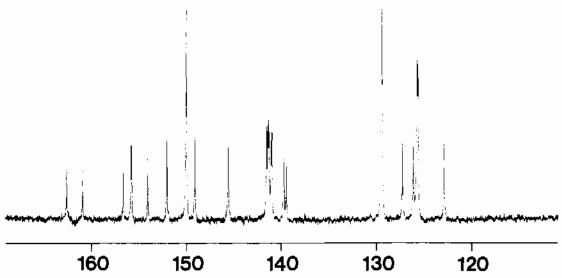

Figure 4. 125-MHz $^{13}C\{^1H\}$ NMR spectrum of $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}$ in $Me_2SO\text{-}d_6$ at 30 °C. Chemical shifts are in units of δ.

II). No changes in the visible or ultraviolet absorption bands of $[Ir(Hbpy\text{-}C^3,N')(bpy\text{-}N,N')_2]^{3+}$ were observed in the presence of $Pr(fod)_3$.

The absence of coupling constants and a resonance due to a proton in the 3-position of the A ring in the ^1H NMR spectrum strongly supports the occurrence of an Ir–C bonded structure in $Me_2SO\text{-}d_6$ and in ACN-d_3 analogous to the solid-state structure.[5] The NMR result could also be attributed to a very labile A-3 proton and a rapid proton exchange at this position in an unbonded pyridine ring (monodentate bpy structure). Indeed, some degree of lability at this position has been reported[8] on the basis of ^1H NMR studies of H–D exchange in $[Ru(bpy)_3]^{2+}$. However, it is unlikely that the Ir–C bond reported for the crystalline solid could be broken in a nonelectrophilic solvent such as $Me_2SO\text{-}d_6$ to yield an unbonded pyridine ring deficient in an A-3 proton. Weak acidity of the positions 3 and 3′ in metal bipyridine complexes may be a general phenomenon that in some cases (such as the Ir complex reported here) leads to intramolecular metalation. This appears to be the first example of metal–carbon bonding in a complex of 2,2′-bipyridine, although a square-planar cyclometalated complex of platinum(II) with *N*-methyl-2,2′-bipyridinium has recently been reported.[9] The effects of $Pr(fod)_3$ suggest a site of Lewis basicity in the complex, consistent with the presence of an uncoordinated N atom in one pyridine ring. The sensitivity of the A-ring proton resonances to the shift reagent indicates that this is the ring that contains the uncoordinated N atom, in agreement with coordination of the A ring via Ir–C bonding. We note that the routine[2,10] use of high-field proton resonances (i.e., chemical shifts upfield of δ 7.2) as a symptom of covalent hydration in metal–bpy complexes is discredited in this analysis. Rather, in this case, they result from shielding effects associated with protons in a metalated pyridine ring.

The proton NMR spectrum changes dramatically in samples in 10^{-4}–10^{-2} M DCl, especially in the high-field end of the spectrum. As the pD of the solution is lowered, high-field resonances (assigned to protons A-4 and A-5) move downfield. These solvent pD effects occur at pD values near the pK_a of the complex (3.0).[3] Deuteration of the A ring may induce a change in conformation of the complex. Changes in the spectrum would result from inductive effects of a deuterated N atom and possibly from equilibration with other tautomeric forms of the complex.[11]

The sensitivity of the A-ring resonances to temperature and solvent (Table II) is consistent with the effects of these parameters on acid–base and conformational equilibria. In nonaqueous solvents the acidic proton associated with the A ring exchanges rapidly between basic sites in the solution: the complex, solvated waters of crystallization, and solvent. The position of the A-ring resonances in different media reflects the point of the resultant acid–base equilibrium as well as solvent and temperature effects on any equilibrium of tautomeric forms.

Carbon-13 NMR. The $^{13}C\{^1H\}$ NMR spectrum obtained at 125 MHz consists of 23 distinct resonances (Figure 4); the chemical shifts of these resonances are independent of applied field strength. Single-frequency off-resonance decoupling indicates that all but seven of these show strong proton (one-bond) coupling. Six of these nonprotonated carbons resonate at the low-field end of the spectrum (δ 154.1–162.6), near the chemical shift of the bridging 2- and 2′-carbons of $[Ir(bpy)_3]^{3+}$.[1,14] We assign the seventh nonprotonated carbon, which resonates at δ 139.5, to carbon A-3 bonded to the iridium metal center. This assignment is made on the basis of the absence of a strong proton coupling and the position of the resonance upfield of those due to bridging 2- and 2′-carbons. No splitting of the ^{13}C resonance by the spin $^3/_2$ iridium nuclei is evident.

Concerning the degeneracy of several carbon-13 shifts, we point to the near degeneracy of several sets of proton chemical shifts (see Table I): (i) Protons C-3, C-3′, C-3″, and D-3 all appear at low field. When, in off-resonance decoupling, the decoupler frequency is to low field of the proton resonances, carbon resonances at δ 125.6 and 125.8 split less than do the other peaks. This is consistent with their being due to carbons C-3, C-3′, C-3″, and D-3. (ii) Protons 4 of the C rings and of the D ring are nearly degenerate. (iii) Protons 5 of the C rings and of the D ring resonate very near one another. These results indicate the near equivalence of corresponding proton sites and of corresponding carbon sites in the C and D rings.

We note with interest that other values reported for the chemical shifts of aromatic carbons bound to iridium(III) are between δ 152.2 and 158.1.[15] These are all hydride complexes.

Acknowledgment. This work was supported by the Division of Basic Energy Sciences of the Department of Energy, Project DE-AT03-78ER70277. High-field spectra were obtained at the Southern California Regional NMR Facility, supported by NSF Grant CHE7916324A1. We thank Dr. W. R. Croasmun and Dr. L. Mueller for their assistance in obtaining these spectra. We thank Professor Nick Serpone for many helpful discussions.

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