Supplementary Material Available. The whole of the Experimental Section of this paper will appear following these pages in the microfilm edition of this volume of the journal. The Experimental Section contains a description of the instrumentation and the details of the preparation and isolation of all of the compounds listed in Tables I–III, as well as the optically active species. In addition, the Experimental Section contains a description of the morphologies of the crystals, the optical rotations, and the analytical data. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50271C-12-75.

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Carbon-13 Nuclear Magnetic Resonance Studies of Platinum(II) Complexes. I. Five-Membered Rings Formed by Substituted 1,2-Diaminoethanes

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The ^{13}C NMR spectra of a series of aqueous square-planar platinum(II) chelates, Pt(bpy)(substituted 1,2-diaminoethane)²⁺, have been obtained for 13 different diamines. ^{13}C chemical shifts of the bipyridine carbons are fairly constant across this entire series; in chelates of nonsymmetric diamines nonequivalent resonances are found for the two bipyridyl rings. ^{13}C resonances of the aliphatic diamine portion resemble those of the free ligand with carbons α to the nitrogen donors showing a 2–10-ppm downfield shift due to platinum binding. Platinum–carbon spin coupling interactions are generally seen for the diamine carbons. $^2J_{PtC}$ for *N*-methyl carbons varies from 10 to 25 Hz, decreasing for *N,N*-dimethyl substitution. $^3J_{PtC}$ values of 20–50 Hz were observed; these data and the known conformational properties of gauche five-membered diamine rings suggest a Karplus-like dependence for $^3J_{PtC}$. Using this $^3J_{PtC}$ information and complementary $^3J_{HH}$, $^3J_{PtH}$, and $^4J_{PtH}$ data an analysis of the conformational properties of gauche 1,2-diamine chelate rings of 1,2-diaminopropane (pn) and its two *N,N*-dimethyl-substituted analogs (*N,N*-Me₂pn) was made. Substantial preference for *C*-methyl equatorial orientation is indicated for pn and N^1,N^1-Me₂pn complexes; N^2,N^2-Me₂pn has nearly equal distribution of axial and equatorial *C*-methyl conformers. Coupling of platinum to the carbon nuclei forming the five-membered rings is highly structurally dependent, being near zero in symmetric rings but 10–15 Hz in unsymmetrical diamine chelates. These observations are explained via a multipath coupling mechanism. Model compounds designed to exclude multipath coupling mechanisms support this type of analysis. ^1H spectra measured at various frequencies from 30 to 300 MHz illustrate a pronounced broadening of platinum satellites at higher fields; at 300 MHz platinum satellites are broadened beyond recognition.

Introduction

Ever since Karplus' classic 1959 paper on the dihedral angle dependence of the three-bond vicinal coupling constant, $^3J_{H–H}$, in H–C–C–H fragments,[2] chemists have attempted to establish molecular geometries from NMR coupling constants. Considerable success has been achieved in extending the Karplus model to analyze empirically variation in coupling constants with dihedral angle in other four-atom fragments.[3] In particular, the dihedral angle dependence of $^3J_{Pt–H}$ in Pt–N–C–H fragments in amino acid chelates was shown to parallel reasonably closely the Karplus curve for $^3J_{H–H}$.[4] More extensive studies of diamine and amino acid complexes of platinum confirmed the earlier suggestions and also established a parallel dependence of $^4J_{Pt–H}$, in Pt–N–C–CH₃ fragments, on the dihedral angle between the Pt–N and the C–C bonds.[5,6] $^4J_{PtH}$ appears to be relatively large (~7 Hz) for ϕ = 180° and to drop off rapidly with decreasing angle.

With the availability of spectrometers capable of obtaining

^{13}C NMR spectra of natural-abundance samples, parallel studies to establish the dihedral angle dependence of $^3J_{Pt–C}$ for coupling between ^{13}C (I = $^1/_2$, 1% abundance) and ^{195}Pt (I = $^1/_2$, 33% abundance) have become feasible. In proton-decoupled carbon-13 spectra, $^3J_{C–Pt}$ can be determined readily as the spacing between the doublet satellites which surround the singlet signal from each different carbon. Thus, if a relatively simple relation between $^3J_{Pt–C}$ and dihedral angle could be established, conformational information for platinum chelates could be obtained readily from ^{13}C spectra as is suggested by a recent ^{13}C study of platinum chelates of *meso*- and *rac*-2,3-diaminobutanes.[7] In view of the difficulty encountered in trying to decipher platinum–proton coupling superimposed on already complex proton-coupled multiplets present in many chelates, ^{13}C–^{195}Pt coupling could offer a much more straightforward approach to conformational studies of platinum complexes.

In addition to this simplifying feature, coupling of platinum

to carbon nuclei provides a different framework on which to gauge molecular geometry. It is expected that $^3J_{PtH}$ and $^3J_{PtC}$ data will give mutually complementary information: $^3J_{PtH}$ indicates the orientation of a proton in a Pt–N–C–H network; $^3J_{PtC}$, that of a CH_3 in the Pt–N–C–CH_3 fragment. In some chelates a lack of suitable proton probes may make ^{13}C NMR the method of choice.

In order to explore the dihedral angle dependence of $^3J_{Pt–C}$, we have prepared and examined ^{13}C spectra of square-planar platinum(II) complexes of three families of chelating ligands for which extensive proton NMR data are available.[5,6] This paper deals with chelates of 1,2-diaminoethanes whose ring stereochemistry is rather well understood in terms of simple, puckered δ and λ conformers (**1**) containing pseudoaxial and

1
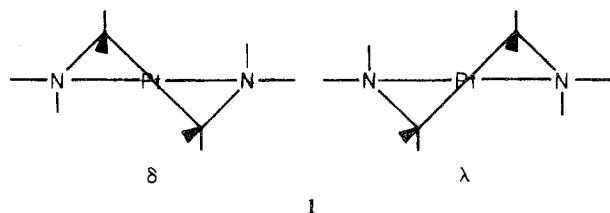
pseudoequatorial substituents.[8–11] Subsequent papers will treat complexes of substituted 1,3-diaminopropanes which form six-membered ring chelates (part II) and methyl-substituted glycinates (part III). For diamine chelates, the effects of out-of-plane interligand interactions have been reduced by examining mixed cationic bipyridyl–diamine chelates, **2**. Use

2
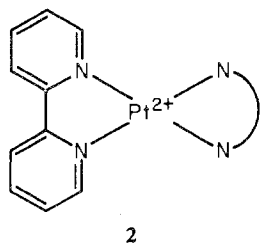
of a cationic complex also permits adjustment of the counter anion to achieve the required high solubility in D_2O.

Although the primary concern in this paper is with conformational implications of $^3J_{Pt–C}$ values, the variation of chemical shifts of ligand carbons and the effect of substitution on coupling between ^{195}Pt and bipyridyl ligand carbons are found to provide sensitive probes to substituent effects on Pt–N bonding in these complexes.

Experimental Section

Diamines. Most of the diamines were obtained commercially from Aldrich Chemical Co. and used without further purification. N^1,N^1-Dimethyl-1,2-diaminopropane and N^2,N^2-dimethyl-1,2-diaminopropane were obtained from Ames Laboratory. The butanediamines were obtained as a meso–racemic mixture from Wyandotte Chemical Co. Isomer separation was achieved by fractional crystallization of the dihydrochloride salts.[12] Synthesis of 2,3-diamino-2,3-dimethylbutane was achieved by reduction of 2,3-dinitro-2,3-dimethylbutane with tin and HCl.[13] 2-Aminomethylpiperidine was prepared from 2-aminomethylpyridine (Aldrich) by hydrogenation of an aqueous pH 1 solution at 50 psi over platinum. Full hydrogenation takes approximately 12 hr and can be monitored by NMR spectra viewing the disappearance of the aromatic protons.

Preparation of Mixed Complexes. The mixed diamine–bipyridyl complexes were prepared by reaction of solid Pt(bpy)Cl_2 with an aqueous solution of the diamine as described earlier,[14] except that, after solvent evaporation, addition of ethanol was used in most cases to precipitate the dichloro salt and remove excess unreacted diamine.

Preparation of NMR Samples. Solutions for NMR analysis were prepared by dissolving 1.5 mmol of solid chloride salt in 3 ml of D_2O. For complexes whose chlorides were not sufficiently soluble, conversion to the more soluble fluoride salt was achieved by passing a saturated aqueous solution of the chloride salt through an anion-exchange column

in the fluoride form. The effluent was then rotary evaporated to dryness and the solid was dissolved in D_2O.

NMR Spectra. Proton NMR spectra of all samples were recorded at 60 MHz (Varian A-60 or Perkin Elmer R-12B spectrometer). Spectra of some samples were also recorded at 30 MHz (Varian EM300) and at 100 MHz (Varian XL-100). For four of the complexes, 300-MHz proton spectra were provided by the NMR spectroscopy laboratory of the Polymer Institute of the University of Akron. Proton chemical shifts were measured relative to the prominent peak (due to bpy H_3) invariably observed near the center of the complex downfield pattern of bipyridyl ring proton signals. This peak was found to have a shift of 8.43 ppm vs. internal DSS in several samples. Although DSS was not added to all samples, this indirect method of shift calibration was employed. Thus, internal shifts are accurate to ±0.03 ppm, but shifts relative to internal DSS may vary by as much as ±0.1 ppm in some cases. FT carbon-13 spectra were obtained at 25.2 MHz with broad-band proton decoupling on a Varian XL-100 spectrometer employing the solvent deuterium signal as an internal lock. A total of 8000–15000 FID's (32000 points) were ensemble averaged to provide the desired signal to noise ratio in the 5-kHz frequency spectra. Pulse angles of 30° were employed with no pulse delay. Ambient temperature was 32°C. Two-drop amounts of dioxane were added to these aqueous solutions as an internal reference. Under these dilute aqueous conditions dioxane is found to have a shift of 67.73 ppm downfield from TMS sealed in an external capillary.

Results

Proton and carbon NMR spectra of the complexes summarized in Table I are all consistent with their formulation as 1:1 mixed chelates. ^{13}C NMR shifts are especially sensitive to the nature of the complex, distinguishing readily the cis and trans forms of the platinum chelate of N,N'-dimethylethylenediamine.

^{13}C **Spectra.** Typical features of the carbon-13 spectra of these compounds are illustrated by the spectrum of a 0.5 M D_2O solution of [Pt(bpy)(N^1,N^1-Me$_2$pn)]Cl_2, which is shown in Figure 1. Assignment of the downfield peaks associated with carbons 2, 4, and 6 of the bpy ring is facilitated by comparison with data for 2-substituted pyridines.[15] Differentiation between the C_3 and C_5 resonances could not be unambiguously made on the basis of such model compounds but was achieved by looking at the proton-undecoupled spectrum. The C_3 carbon showed long-range coupling of 8 Hz splitting its resonance into a doublet of doublets. Long-range coupling to C_5 was much more complex. These observations agree with long-range $^1H–^{13}C$ coupling seen in other pyridines.[16] The diminished intensity of the C_2 signals is typical in the series studied here and is directly attributable to saturation effects associated with the long T_1 of a nonprotonated carbon atom.[17] As evident in the expanded trace for C_2 and $C_{2'}$, Figure 1, each of the peaks, except C_4, is surrounded symmetrically by platinum-195 satellites whose spacings yield $J_{Pt–C}$ for the corresponding carbon. As expected, five resonances are distinguished for the aliphatic ring protons. Generally these resonances were assigned on the basis of internal consistency in the entire series studied and through the well-established axioms governing ^{13}C shifts, i.e., effects of electronegative substituents, and known downfield shifts due to substitution α and β to a given carbon atom.[15] Where any doubt about an assignment could exist, as in the spectrum depicted in Figure 1, off-resonance proton-decoupled ^{13}C spectra were obtained to characterize the spectrum. As can be seen from Table I individual diamine ring carbons show different coupling to the platinum nucleus; the C-methyl carbon in Figure 1 provides an especially vivid example of such platinum interaction.

On the basis of the natural abundance of platinum-195 the carbon signals are expected to show a 1:4:1 intensity pattern due to platinum coupling. However the satellites always appear somewhat broader giving the center band more relative
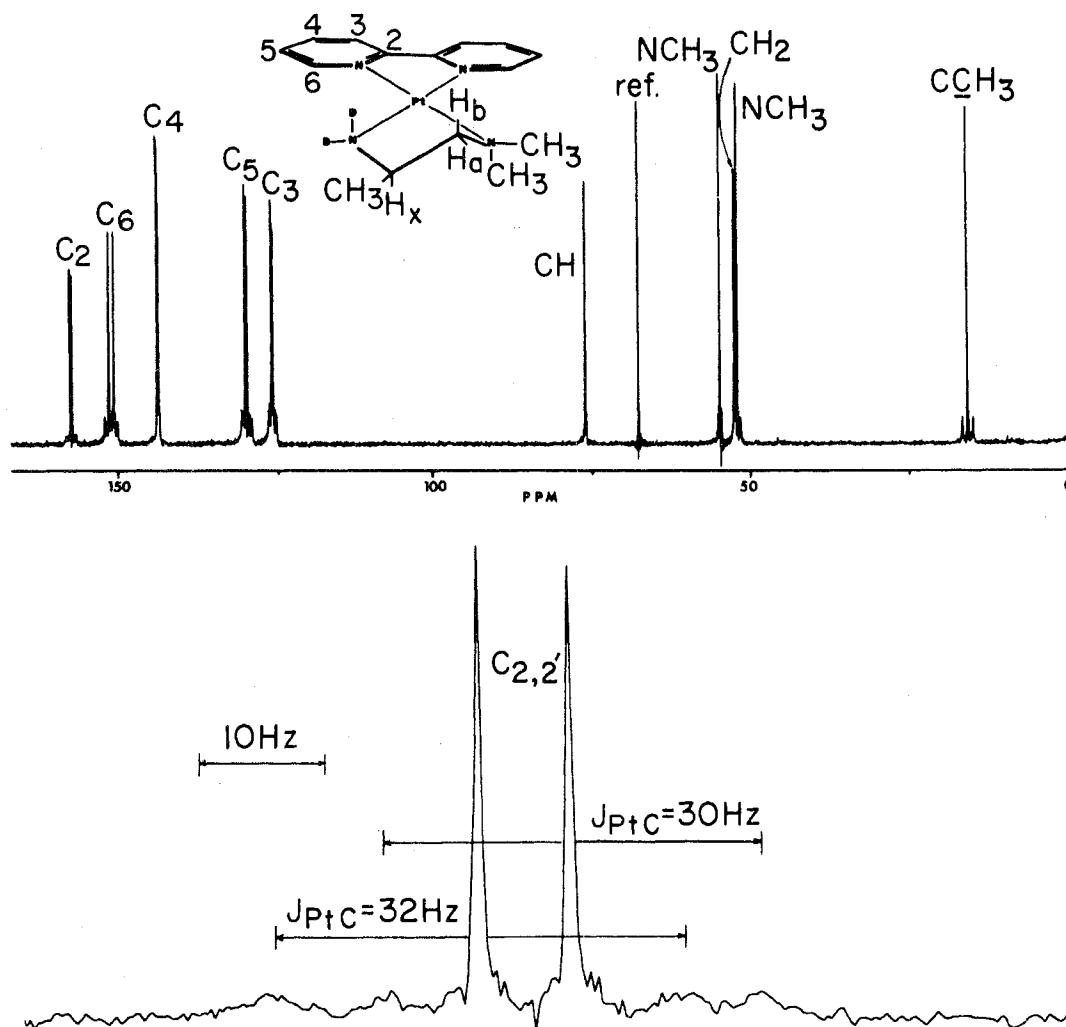
Figure 1. The 25.2-MHz ^{13}C NMR spectrum of Pt(bpy)(N^1,N^1-Me$_2$pn)$^{2+}$; reference is 1,4-dioxane. Bottom shows expanded-scale plot of bipyridine C_2 resonances and platinum satellites.

height. Such observations have been made previously.[18] In some cases the broadening was too great or the splitting too small to permit determination of J_{Pt-C}.

Proton Spectra. The proton NMR spectrum of [Pt-(bpy)(N^1,N^1-Me$_2$pn)]Cl$_2$, shown in Figure 2, is typical of the proton spectra of these complexes. In the 60-MHz trace, the C–CH$_3$ doublet and N–(CH$_3$)$_2$ peaks are clearly evident at 1.59 and 3.25 ppm, respectively. The ^{195}Pt satellites of the N(CH$_3$)$_2$ peak ($^3J_{Pt-H}$ = 31 Hz) are quite prominent, but the ^{195}Pt satellites of the C–CH$_3$ doublet ($^4J_{Pt-H}$ = 4.1 Hz) are less distinct. Like all of the mixed diamine–bipyridyl complexes, the aromatic ring part of the spectrum consists of three characteristic parts. The broad doublet at 8.87 ppm is assigned to H$_6$ which is coupled strongly to H$_5$ and only weakly to H$_4$ and H$_3$. The observation of a downfield ^{195}Pt satellite doublet ($^3J_{Pt-H}$ = 26 Hz) distinguishes this doublet from the doublet of H$_3$, which would normally be expected to be at higher fields. The high-field ring multiplet at about 7.9 ppm is assigned to H$_5$, which identifies the more intense unresolved multiplet whose most prominent peak is at 8.43 ppm as due to H$_3$ and H$_4$. Although protons meta to nitrogen are most shielded in pyridine,[19] for chelated bipyridyl one meta proton (H$_3$) is shifted downfield under the influence of the ring current of the other ring.

Details evident in the 300-MHz spectra, in Figure 2, confirm these assignments and permit determination of spin coupling constants for diamine ring protons. At 300 MHz, bipyridyl ring proton peaks of H$_6$ and H$_5$ are clearly separated into two

doublets (H$_6$) or triplets (H$_5$), reflecting the nonequivalence of the rings. However, the separation between H$_3$ and H$_4$ is still quite small. The ABCX$_3$ pattern for the diamine ring protons (ABC), which is barely visible near the prominent N(CH$_3$)$_2$ peak at 60 MHz, is clearly resolved at 300 MHz into approximately a first-order pattern with additional coupling of H$_X$ to C–CH$_3$. Similar first-order spectra were obtained for the pn and N^2,N^2-Me$_2$pn complexes at 300 MHz. Values for $^3J_{H-H}$ and $^2J_{H-H}$ were obtained from these spectra.

An additional complication is introduced by going to higher magnetic field strengths. A systematic increase in line width of ^{195}Pt satellites is observed as the field strength is increased. Whereas at 30 MHz, the ratio of parent peak heights to corresponding ^{195}Pt satellite peak heights is nearly the 4:1 value expected for 33% abundance of ^{195}Pt, at 60 MHz, the ratio is about 5:1; at 100 MHz, the ratio is about 7:1. In the 300-MHz spectra, the satellites are too broad to permit reliable location. For example, the complete lack of ^{195}Pt satellites for the strong N(CH$_3$)$_2$ peak (still only one peak for the nonequivalent N-methyl groups even at 300 MHz) is particularly striking. Unfortunately, this broadening of ^{195}Pt satellites prevented us from determining reliable values for $^3J_{Pt-H}$ for en-ring protons of the three pn ligands whose 300-MHz proton spectra were recorded. Such line broadening at high fields appears to limit the utility of high-field spectra for determining $^3J_{Pt-H}$. As noted earlier similar broadening of ^{195}Pt satellites of ^{13}C resonances is also observed at 25.2 MHz (23.4 kG). Further investigation of this field dependence

Table I. Proton and Carbon NMR Chemical Shifts^{a,b} and Coupling Constants (^{195}Pt–^{1}H and ^{195}Pt–^{13}C) for Pt(bpy)(1,2-diamine)$^{2+}$ Complexes

Compd	Diamine structure	Carbon-13 resonances — bpy: C_2	C_6	C_4	C_5	C_3	Diamine ring carbons	C-CH$_3$	N-CH$_3$	Proton resonances — bpy: $H_{3,3'}$	$H_{4,4'}$	$H_{5,5'}$	$H_{6,6'}$	Diamine ring CH, CH$_2$	C-CH$_3$	N-CH$_3$
Pt(bpy)(en)$^{2+}$		156.93 (32)^c	151.62 (32)	142.97 (6)	129.52 (34)	125.19 (27)	48.33 (NO)^d			8.43	8.43	7.86	8.70 (32)^c	3.01 (40)		
Pt(bpy)(pn)$^{2+}$		156.66 (31)	151.70 (32) 151.34 (32)	142.97 (6)	129.67 (34)	125.07 (26)	56.42 (CH) (NO) 52.97 (CH$_2$) (6)	17.05 (38)		8.43	8.45 8.43	7.85	8.65 (32) 8.62 (32)	2.82 (A)^e 3.45 (X)^e 3.14 (B)^e	1.60 (~2)^k	
Pt(bpy)(ms-bn)$^{2+}$		156.62 (30)	151.58 (33)	143.09 (5)	129.75 (33)	124.99 (26)	58.09 (NO)	14.40 (26)		8.43	8.43	7.98	8.75 (32)	3.53 (39)	1.55 (NO)	
Pt(bpy)(rac-bn)$^{2+}$		157.25 (30)	151.22 (29)	142.85 (6)	129.40 (34)	125.15 (26)	60.31 (NO)	18.44 (51)		8.43	8.46	7.85	8.67 (31)	3.01 (9)	1.47 (NO)	
Pt(bpy)(C,C-Me$_2$en)$^{2+}$		157.29^f	151.74 (32) 151.02 (32)	142.85 (6)	129.28 (35)	125.15 (27)	61.77 (C)^g (NO) 56.86 (CH$_2$)^g (8)	24.83^g (22)		8.43	8.43	7.85	8.60 (33)	2.92 (43)	1.58 (<2)^k	
Pt(bpy)(C,C-,C',C'-Me$_4$-en)$^{2+}$		157.10 (28)	151.38 (32)	142.77	129.16 (34)	124.99 (26)	65.23 (NO)	23.84 (24)		8.43	8.43	7.91	8.77 (32)		1.57 (<2)^k	
Pt(bpy)-(cyda)$^{2+}$		157.09 (33)	151.42 (32)	142.89	129.56 (34)	125.15 (28)	62.77 (α-CH) (NO) 33.37 (β-CH$_2$) (52) 25.11 (γ-CH$_2$) (NO)			8.43	8.52	7.95	8.73 (34)	2.88 (X)^h		
Pt(bpy)(N-Meen)$^{2+}$		156.73 (32)	151.66 (32) 151.30 (31)	143.21 (7)	129.91 (34) 129.60 (34)	125.27 (27) 125.19 (26)	58.56^g (NH) (10) 44.16^g (NH$_2$) (7)		41.74^g (23)	8.43	8.43	7.88	8.80 (32) 8.65 (32)	3.33		3.11 (39)

13C shifts (ppm; Pt–C coupling, Hz, in parentheses)

Compound	C (~157)	C (~150)	C (~143)	C (~129)	C (~125)	CH₃ / other	NCH₃ / CH	CH₂ / NH
Pt(bpy)(N,N'-Me₂-en)²⁺ (cis/trans)	156.96 (32)	151.30 (31)	143.33 (6)	129.79 (33)	125.31 (27)		54.71 (trans) (NO), 56.46 (cis) (NO)	42.33 (trans) (20), 43.40 (cis) (24)
Pt(bpy)(N,N-Me₂en)²⁺	157.53^f, 157.25^f	150.98 (33), 150.39 (28)	143.40 (6)	129.48 (32), 129.24 (35)	125.47 (28), 125.27 (26)		53.09 (15)	71.42 (N) (11), 45.23 (NH₂) (13)
Pt(bpy)(N,N,N'-Me₃-en)²⁺	157.29 (33), 157.02 (32)	151.10 (34), 150.55 (28)	143.72, 143.64	129.75 (34), 129.60 (30)	125.55 (26), 125.39 (26)		54.87^g (10), 52.49^g (22), 42.41^g (NH) (24)	67.81^g (N) (NO), 54.67^g (NH) (10)
Pt(bpy)(N²,N²'-Me₂-pn)²⁺	157.69^f, 157.37^f	150.71 (34), 150.11 (26)	143.37, 143.35	129.36 (31), 129.12 (35)	125.51 (28), 125.31 (26)	9.79 (20)	52.21^g (16), 45.71^g (23)	74.63^g (CH) (12), 49.28^g (CH₂) (14)
Pt(bpy)(N¹,N¹'-Me₂-pn)²⁺	157.29 (32), 157.02 (30)	151.18 (34), 150.39 (28)	143.49, 143.40	129.56 (30), 129.32 (34)	125.47 (27), 125.27 (26)	16.06 (43)	54.83^g (8), 52.13^g (11)	52.57^g (CH) (8), 76.10^g (CH₂) (NO)
Pt(bpy)(NH₃)₂²⁺	157.29^f	149.87 (34)	142.97 (6)	129.16 (35)	125.23 (28)			
Pt(bpy)(NH₂CH₃)₂²⁺	157.02^f	149.79 (32)	143.17 (~5)	129.52 (NO)	125.23 (26)	34.91 (24)		

1H shifts (ppm; coupling, Hz, in parentheses)

Compound					ligand H
Pt(bpy)(N,N'-Me₂-en)²⁺ (cis/trans)	8.43	8.48	7.90	8.76 (32)	2.93; 3.20 (40)
Pt(bpy)(N,N-Me₂en)²⁺	8.43	8.33	7.85	8.56 (30), 8.87 (27)	3.15 (36); 3.30 (30)
Pt(bpy)(N,N,N'-Me₃-en)²⁺	8.43	8.43	7.93	8.84 (26), 8.75 (NO)	3.44; 2.95 (31), 3.21, 3.25 (36), 3.25 (NO)
Pt(bpy)(N²,N²'-Me₂-pn)²⁺	8.43	8.38	7.88	8.89 (26)	3.11 (A,B)^i, 3.54 (X)^i; 3.17 (30); 1.53
	8.43	8.51	8.00	8.64 (32)	3.37 (30); (<2)^k
Pt(bpy)(N¹,N¹'-Me₂-pn)²⁺	8.43	8.36	7.85	8.87 (26)	3.14 (A)^j, 3.64 (X)^j; 3.25 (31); 1.59 (4.1)
	8.43	8.55	7.99	8.48 (NO)	3.04 (B)^j
Pt(bpy)(NH₃)₂²⁺	8.43	8.43	7.88	8.70 (35)	
Pt(bpy)(NH₂CH₃)₂²⁺	8.43	8.43	7.99	8.75 (32)	2.90 (44)

^{a} Carbon-13 shifts in ppm from external TMS; measured vs. internal dioxane which is 67.73 ppm downfield from external TMS. ^{b} Hydrogen-1 shifts in ppm vs. DSS (see Experimental Section). ^{c} Coupling constants (Pt–H and Pt–C) are found in parentheses; in Hz. ^{d} NO indicates platinum satellites not observed. ^{e} $J_{AB} = 12.0$ Hz, $J_{AX} = 9.0$ Hz, and $J_{BX} = 4.5$ Hz, obtained from 300-MHz spectra. ^{f} Signal saturation prohibited determining $^2J_{Pt-N-C}$. ^{g} Assignments based on off-resonance decoupled spectra. ^{h} Other multiplets are observed at 2.44, 1.89, 1.70, and 1.47 ppm. ^{i} $J_{AX} = J_{BX} = 7$ Hz, obtained from 300-MHz spectra. ^{j} $J_{AX} = 12$ Hz, $J_{BX} = 4$ Hz, and $J_{AB} = 12$ Hz, obtained from 300-MHz spectra. ^{k} Satellites not actually resolved, but limits or approximate values of J estimated from line shapes.
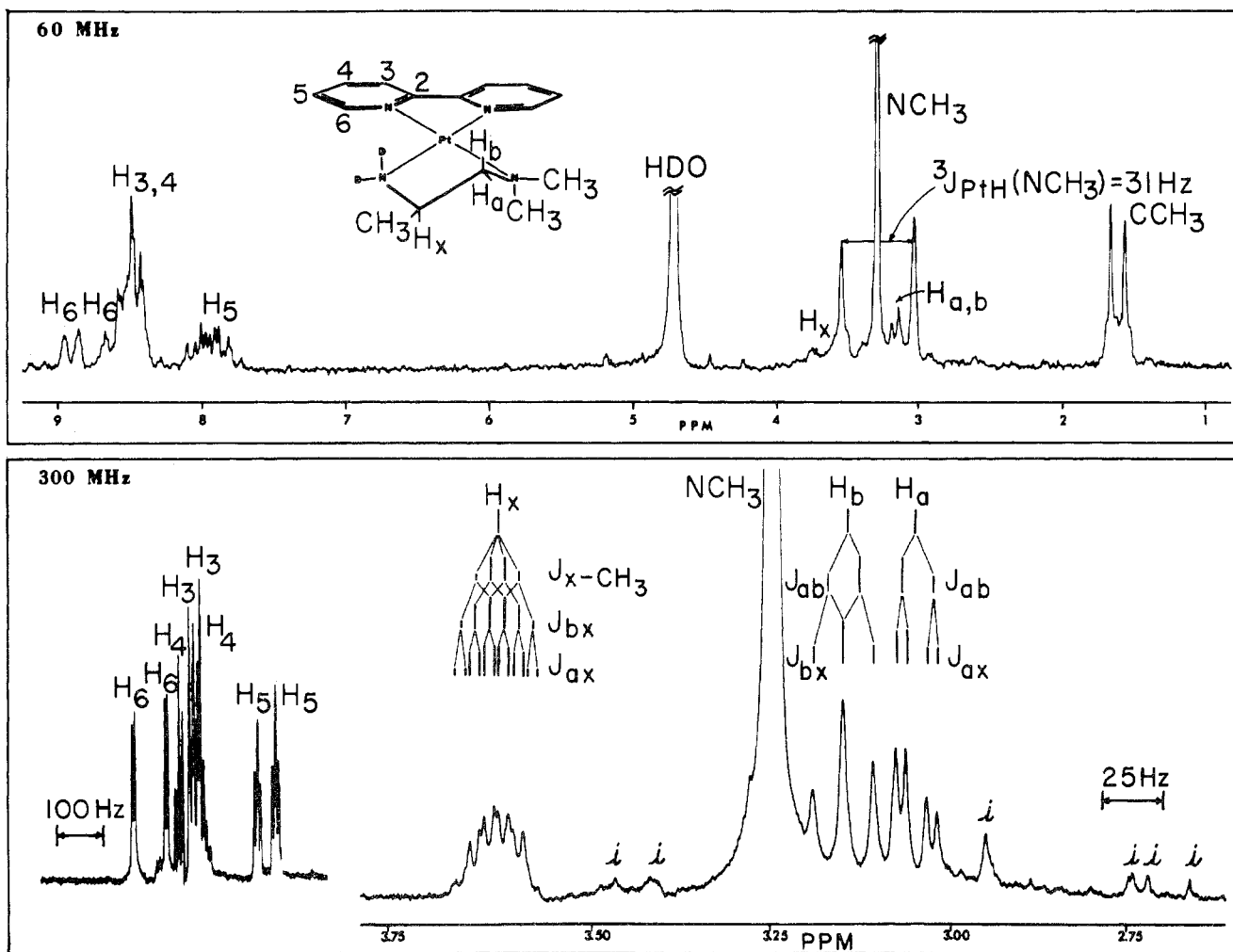
Figure 2. Top: 60-MHz ^{1}H NMR spectrum of Pt(bpy)(N^1,N^1-Me$_2$pn)$^{2+}$ in D$_2$O. Bottom: 300-MHz expansions of aromatic protons and diamine protons (i = impurity).

of platinum-195 relaxation is under way.

Discussion

$^2J_{Pt-C}$ **in N–CH$_3$ Fragments.** For N-methyl-substituted diamines, values for $^2J_{Pt-C}$ lie in the range of 10–25 Hz. These values are consistent with those observed for $^2J_{Pt-C}$ for analogous complexes of methyl-substituted ammonia. Increased methyl substitution generally leads to a decrease in $^2J_{Pt-C}$ for coupling to N–CH$_3$ carbon. This is paralleled by a decrease in coupling to the CH$_3$ protons and by a decrease in coupling between Pt and C$_6$ as well as Pt and H$_6$ of one of the two bipyridyl rings.

It should be noted that there is normally an alternation in the sign of J with each additional σ bond between the coupled atoms.[20] In the following discussion, we will assume that $^2J_{Pt-C}$ and $^3J_{Pt-C}$ have opposite signs.
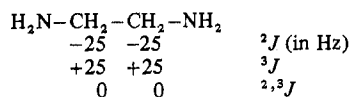
$^3J_{Pt-C}$ **in Pt–N–C–CH$_3$ Fragments.** Coupling between Pt and C–CH$_3$ carbons is typically somewhat greater than $^2J_{Pt-C}$ to N–CH$_3$ carbons. However the variation is much greater, with values ranging from 20 to 52 Hz for the eight members of the series. Clearly this reflects the variation in ligand conformation of the diamines. If the variation of $^3J_{Pt-C}$ with dihedral angle follows a Karplus-type (cos^2 ϕ) curve, the largest observed values (52 Hz) should correspond most closely to an equatorial orientation ($\phi = 160°$ for five-membered rings). Similarly, a pure axial orientation ($\phi = 90°$) would be expected to have a very small value for $^3J_{Pt-C}$, perhaps approaching zero. Intermediate coupling would be expected
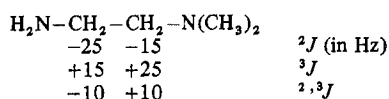
if both axial and equatorial orientations are important.

Data for the eight members of this series can be understood readily in terms of this model. In chelated cyda, the β carbon is necessarily equatorial, and $^3J_{Pt-C}$ = 52 Hz. The similar value observed for rac-bn suggests that it has a similar conformation, with both CH$_3$ groups equatorial. By contrast, in the ms-bn complex, a particular methyl group has equal probability of being either axial or equatorial, with rapid δ ⇌ λ conformational interchange yielding a time-averaged environment between the two states. The observed average coupling constant of only 26 Hz suggests that $^3J_{Pt-C}$ for an axial methyl group is close to zero, as required by the Karplus relation with $\phi = 90°$. Our data and conclusions are in agreement with the similar interpretation of parallel data for analogous complexes, Pt(NH$_3$)$_2$(rac- or ms-bn)$^{2+}$, reported recently by Bagger.[7] Similar but somewhat smaller values for $^3J_{Pt-C}$ are observed for the other two symmetric members of the series, C,C-Me$_2$en (21 Hz) and C,C,C',C'-Me$_4$en (24 Hz). Those values are again near the average of J_{ax} (~0) and J_{eq} (~52 Hz). However, for the pn complex, $^3J_{Pt-C}$ is again relatively large (38 Hz) consistent with substantial, but not complete, preference for equatorial methyl group orientation. Interestingly, the effect of dimethyl substitution at the two nitrogens is quite different. Substitution at N^1 produces a slight increase in $^3J_{Pt-C}$ (to 43 Hz for N^1,N^1-Me$_2$pn), but substitution at N^2, a substantial decrease in $^3J_{Pt-C}$ (to 20 Hz for N^2,N^2-Me$_2$pn). The former, like pn, apparently also prefers the conformation with C–CH$_3$ equatorial. For the latter, steric

interaction between N(CH₃)₂ and C–CH₃ is relieved by an axial orientation for C–CH₃ which may even be the favored conformation.

$^{2,3}J_{Pt-C}$ **for en-Ring Carbons.** We were at first puzzled that coupling between ^{195}Pt and en-ring carbons was much smaller than coupling to C–CH₃ or N–CH₃ carbons which were separated by the same number of bonds. However, the small values can be understood readily if one recognizes that the observed coupling to ring carbons is a sum of the two-bond coupling through one nitrogen and the three-bond coupling through the other nitrogen. In σ-bond networks ^2J and ^3J are expected to possess opposite signs.[20,21] We have not performed relative sign determinations for the coupling constants cited in this paper but for sake of argument will assume $^2J_{PtNC}$ is negative[25] as has been established for $^2J_{Hg-C-C}$ and $^2J_{Sn-C-C}$.[26] Coupling of platinum-195 to the ring ^{13}C nuclei proceeds by two oppositely signed paths diminishing the observed value of this interaction (which we designate $^{2,3}J_{Pt-C}$) by cancelation effects. As an example, in Pt(bpy)(en)²⁺, reasonable values of $^2J_{Pt-C}$ and $^3J_{Pt-C}$ might well be about –25 and +25 Hz, respectively. The former is consistent with data for the methylamine complex Pt(bpy)(NH₂CH₃)₂²⁺. The latter is a rough estimate for ^3J coupling to ring carbons based on ring Pt–N–C–C dihedral angles and $^3J_{Pt-C}$ data for C-methyl carbons.

$$
\begin{array}{ll}
\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2 & \\
\quad -25 \quad\quad -25 & ^2J \text{ (in Hz)} \\
\quad +25 \quad\quad +25 & ^3J \\
\quad\quad 0 \quad\quad\quad 0 & ^{2,3}J
\end{array}
$$

On the other hand, the platinum complex of N,N-Me₂en shows 11- and 13-Hz platinum coupling to its ring carbons. These numbers can be rationalized by considering a multipath coupling scheme. The magnitudes of both $^2J_{Pt-C}$ and $^3J_{Pt-C}$ are expected to be diminished by progressive N-methyl substitution; evidence for this is derived from our $^2J_{PtCH_3}$ data for N-substituted diamines and also $^3J_{PtNCH_3}$ data for the same compounds (Table I). Similarly Appleton and Hall[27] found that $^3J_{PtNCH}$ in Pt(NH₃)₂(1,3-diaminopropane)²⁺ undergoes a reduction from 43 to 27 Hz upon tetramethylation of the nitrogen donors of the diamine ligand. An analogous decrease in $^3J_{PtNCH}$ is found for platinum–ethylenediamine complexes on nitrogen methylation.[27] From a consideration of these data an adjustment of coupling magnitudes through the tertiary nitrogen is appropriate and is illustrated as follows.

$$
\begin{array}{ll}
\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{N(CH}_3)_2 & \\
\quad -25 \quad\quad -15 & ^2J \text{ (in Hz)} \\
\quad +15 \quad\quad +25 & ^3J \\
\quad -10 \quad\quad +10 & ^{2,3}J
\end{array}
$$

This model accounts reasonably well for the observed coupling magnitudes of ring carbons in the N,N-Me₂en complex and other unsymmetric diamine complexes. Interestingly this model predicts opposite signs for $^{2,3}J$ for the two en carbons.

Two other situations of observable platinum coupling to ring carbons exist where no nitrogen substitution is present, i.e., for the pn and C,C-Me₂en complexes. If we assume that $^3J_{Pt-C}$ values of en carbons are an average of contributions from λ and δ conformations (**1**) and that $^3J_{Pt-C}$ is influenced only by the extent of substitution at nitrogen, $^{2,3}J_{Pt-C}$ should be the same for all en carbons, of all diamine ligands that are not substituted at nitrogen. However, if the degree of puckering of the chelate ring is different for the two conformers, one carbon might easily be more strongly coupled to Pt than the other. Alternatively electronic effects of methyl substitution on the individual $^2J_{PtC}$ and $^3J_{PtC}$ components may account for these small changes.

Conformational Implications of Coupling Constants. The critical NMR data required to evaluate ring conformations

of chelated ethylenediamines are summarized in Table II. Table II also includes sketches indicating at least qualitatively the degree of conformational preference suggested by the NMR data. The basis of these preferences will now be considered.

In the simple λ ⇌ δ equilibrium[8] ring protons or C-methyl groups are then either pseudoaxial (ax) or pseudoequatorial (eq) as noted in Table III for chelated pn. Table III also includes a range of values for the critical NMR parameters for the extreme conformations as estimated from data in the literature.

Application of this model to the data in Table II can be handled most easily by considering the nine compounds in three groups in order of increasing complexity. The first four ligands are symmetric so that ring protons or methyl groups necessarily have the same chance of being equatorial as axial. The observed coupling constants should therefore be an average of values for axial and equatorial orientations. The small range observed for $^3J(Pt-N-C-H)$, 39–43 Hz, and $^3J(Pt-N-C-CH_3)$, 21–26 Hz, supports the validity of this model. Furthermore the J values lie within the range suggested in Table III for an average of axial and equatorial values.

By contrast, for racemic butanediamine (*rac*-bn) and cyclohexanediamine (cyda), a strongly preferred extreme conformation with C–H protons axial is indicated. For cyda, rigidity of the cyclohexane ring ensures this conformation; for *rac*-bn, the close agreement between comparable J values of cyda and *rac*-bn argues strongly for the same conformation.

For the three pn derivatives, the variation in conformational preference is substantial. Both vicinal proton–proton coupling on the ligand and $^3J_{PtC}$ to the C-methyl carbon are consistent with strong preference for the equatorial orientation of C–CH₃ in both pn and N^1,N^1-Me₂pn. For both compounds, $^3J_{Pt-C}$ to C–CH₃ is relatively large (38 Hz for pn and 43 Hz for N^1,N^1-Me₂pn), suggesting preference for equatorial methyl orientation. However, neither value is as large as the 52 Hz observed for both *rac*-bn and cyda. If one assumes that the observed J is an average of axial (~0) and equatorial (~52 Hz) values, weighted according to the relative populations of λ and δ conformers, 38 and 43 Hz indicate 72 and 80% contributions, respectively, for the conformers with CH₃ equatorial. The differences in vicinal $^3J_{HH}$ for the two compounds support the conclusion that conformational preference is strong; the 12 and 4 Hz obtained for N^1,N^1-Me₂pn corresponds very closely (within 0.5 Hz) to values reported by Saito et al. for Co(III), Pd(II), and Pt(II) complexes of pn.[28] If these values can be taken to indicate pure δ conformation (Table III) as these authors suggest, the 9.0 Hz observed for the larger vicinal $^3J_{H-H}$ in pn would correspond to about 65% contribution for the preferred δ conformation. The 9 and 4.5 Hz observed here for pn is very close to values reported for 2:1 Pt(II) complexes of 1,2-diaminopropionic acid.[4] For these diaminopropionic acid complexes, $^3J_{Pt-H}$ data indicate strong preference for equatorial carboxylate in both protonated and unprotonated forms.[4] It is possible that the observed differences in $^3J_{H-H}$ and $^3J_{Pt-C}$ may reflect differences in the degree of puckering of the ring at the conformational energy minimum rather than significant differences in relative amounts of the two conformers. The observation of significant $^4J_{Pt-H}$ coupling to C–CH₃ for N^1,N^1-Me₂pn (4.1 Hz) suggests that the degree of ring puckering may be greater for this complex than for pn ($^4J_{Pt-H}$ ≃ 2, estimated from line shape although satellites are not clearly resolved). The observation of such long-range coupling seems to require something approaching a trans conformation in the Pt–N–C–CH₃ framework.[5,29]

Although conformational preference is strong for both pn and N^1,N^1-Me₂pn, for N^2,N^2-Me₂pn, which has two methyl

Table II. Preferred Conformations of Five-Membered Ring Chelates of Platinum(II) and Supporting NMR Data^a

Ligand	$^3J(H-C-C-H)^b$	$^3J(Pt-N-C-H)^b$	$^3J(Pt-N-C-CH_3)$	$^4J(Pt-N-C-CH_3)$	Preferred conformation
en		42			
C,C-Me$_2$en		43	21	<2	
C,C,C',C'-Me$_4$en			24	<2	
ms-bn	c	39	26	c	
rac-bn	c	9	52	c	
cyda	c	d	52	c	
pn	4.5 (BX) 9.0 (AX)	d	38	~2	
N^1,N^1-Me$_2$pn	4 (BX) 12 (AX)	d	43	<4.1	
N^2,N^2-Me$_2$pn	7 (AX = BX)	d	20	<2	

^{a} All values are given in Hz and correspond to coupling between underlined proton, ^{13}C, or ^{195}Pt. ^{b} Values correspond to coupling involving protons attached to ring carbons only. ^{c} Complex pattern not readily analyzed. ^{d} Values could not be determined from complex 60-MHz spectra; at 300 MHz platinum satellites too broad.

Table III. Conformational Representation and Expected *J* Values (Hz) for Chelated Propanediamine (pn)

Coupling constant	Representative values	Basis
$^3J(H\text{-}C\text{-}C\text{-}H)$	$J(\text{eq-eq}) \simeq 3$	Ref 3
	$J(\text{ax-ax}) \simeq 12$	
	$J(\text{ax-eq}) \simeq 3$	
$^3J(Pt\text{-}N\text{-}C\text{-}H)$	$J(\text{Pt-H}_{ax}) \simeq 15$	Ref 4–6
	$J(\text{Pt-H}_{eq}) \simeq 60$	
$^3J(Pt\text{-}N\text{-}C\text{-}CH_3)$	$J(\text{Pt-C}_{ax}) \simeq 0$	This work, ref 7
	$J(\text{Pt-C}_{eq}) \simeq 50$	
$^4J(Pt\text{-}N\text{-}C\text{-}CH_3)$	$J(\text{Pt-}CH_{3\,ax}) \simeq 0$	Ref 5, 6
	$J(\text{Pt-}CH_{3\,eq}) \simeq 7$	

bpy ^{13}C resonances
C₂: 157.25
C₃: 125.23 (26)
C₄: 143.05
C₅: 129.63 (34), 129.32 (33)
C₆: 151.22 (32), 151.10 (32)

Figure 3. [13]C data for the (bipyridine)(2-aminomethylpiperidine)-platinum chelate. Shifts in ppm vs. TMS; Pt–C coupling constants (in parentheses) in Hz.

groups on the nitrogen adjacent to the C–CH₃ carbon, the data indicate little preference for either conformation. If the observed value of $^3J_{Pt-C}$, 20 Hz, is increased to 27 Hz to correct for the attenuation of methyl substitution at nitrogen, it corresponds to that observed for other symmetric ligands for which no conformational preference is possible. Near equality of vicinal $^3J_{H-H}$ coupling to Hx also supports this conclusion. Apparently, the unfavorable gauche interaction of a C–CH₃ group with two N–CH₃ groups partially compensates for the usual tendency for C–CH₃ to prefer an equatorial orientation. Like all the symmetric ligands, no [195]Pt satellites are observed for C–CH₃ proton signals.

An effort was made to probe the idea of multipath coupling between platinum and carbon nuclei by preparing a diamine chelate having two rings: one capable of multipath coupling and another in which J_{Pt-C} is constrained to a single path. The system utilized was the platinum chelate of 2-aminoethyl-piperidine, Pt(bpy)(pipen)²⁺, shown in Figure 3. This complex is readily seen to be a derivative of ethylenediamine to which a chair piperidine ring has been joined. Like other fused bicyclic ring systems two isomers are possible for such a molecule, cis-fused and trans-fused ring structures.[30] Only six resonances attributable to the chelated aliphatic diamine are visible in the ^{13}C spectrum of Pt(bpy)(pipen)²⁺ indicating the presence of only one isomer. Models suggest that the trans-fused chelate in Figure 3 is sterically more favorable than the cis-fused structure. A similar preference has been demonstrated in the decalin system.[30] Like *trans*-decalin the aliphatic rings of the pipen chelate (Figure 3) are incapable of conformational inversion.

Figure 3 includes a summary of ^{13}C shift and J_{Pt-C} data for the complex. Assignment was made considering the factors described earlier. A tentative assignment of C₃ and C₅ of the piperidine ring was made on the basis of the number of β substituents for each. C₃ has three and C₂ only two; therefore one might expect C₃ to be more downfield. A reversal of this assignment is possible but would not materially affect the ideas presented below.

The coupling $^3J_{PtC_3(pip)}$ of 41 Hz is reasonable for an equatorial substituent on the puckered five-membered ring;

52 Hz was observed for similar carbons in the *rac*-bn and cyda chelates. Coupling of platinum to C₆ of the piperidine ring is found to be 25 Hz. This value represents pure $^2J_{PtC}$, there being only one reasonable bonding framework for these two nuclei to spin couple. $^2J_{PtC}$ agrees well with the geminal coupling constant estimated for our earlier multipath coupling arguments for chelate ring carbon atoms. In the pipen chelate the two five-membered ring carbons show J_{PtC} of 10 and 15 Hz. These nonzero couplings can be ascribed to multipath coupling. The remaining two piperidine carbons, C₄ and C₅, show Pt–C coupling of 30 and 0 Hz, respectively; C₅ is in a vicinal unit with a favorable dihedral angle, and C₄ is four bonds removed from platinum and should exhibit small coupling.
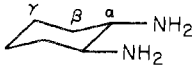
[13]C Chemical Shifts. The shifts of the bipyridyl carbons exhibit a consistent pattern across the entire series of complexes viewed here (see Table I). Their shifts are characteristic of pyridyl units.[15] The shift of C₆ is by far the most sensitive to features of the diamine moiety N,N-Dimethyl-substituted diamine chelates show the most pronounced effects on the bpy C₆ parameters: (1) reducing one $^2J_{PtC_6}$ from typically 32 to 28 Hz and (2) shifting one C₆ resonance upfield by about 0.6 ppm to ~150.4 ppm. Furthermore the upfield shifted C₆ resonance always shows the smaller coupling constant. These observations can be rationalized in terms of the unsymmetrical diamine ring rendering the pyridyl moieties of the bpy unit (3) nonequivalent through steric influence of the dimethyl

3
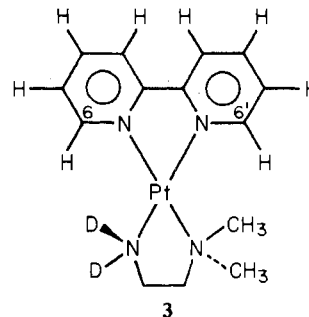
substitution at one amine center. Grant and coworkers[31,32] have shown that methyl groups exhibiting significant non-bonding interactions with nearby CH or CH₃ units, as in axial methyl–cyclohexyl systems or ortho-substituted benzenes, produce pronounced upfield shifts in carbon resonances for the proximate groups. Models indicate that the C₆ proton and amine methyl groups are spatially close and a similar upfield shift might be expected for C₆'. This proximity of the bulky methyl groups and H₆' might also lead to a slight weakening of the Pt–bpy bond cis to the tertiary amine producing a decrease in the observed spin coupling to that ring. Indeed, inspection of the data for complexes of N,N-dimethyl ligands shows analogous carbons of each bpy ring to be coupled slightly differently to the platinum nucleus. Similar effects are observed simultaneously for $^3J_{PtH_6}$ in these systems. Further support for unequal bond strengths in the two pyridyl moieties in these N,N-dimethyl systems is reflected in the observation of two distinct carbon resonances for all five carbons. That these differences in the bpy rings could arise from different trans influences of the –N(CH₃)₂ and –NH₂ donor groups cannot be discounted. Clark and coworkers[33,34] have observed such trans influences in $^1J_{PtC}$ data in methyl and phenyl organometallic compounds.

[13]C spectra of the aliphatic diamine carbons are found to resemble those of the free amines rather closely.[35,36] This suggests that the factors most influential in determining ^{13}C shifts of the complexed ligands are the same as those in the amines: (1) the presence of an electronegative substituent on a carbon atom, (2) the number of carbon atoms directly

Table IV. ^{13}C Chemical Shifts^a for Various 1,2-Diamines and Their Changes upon Protonation and upon Chelation to Form Pt(bpy)(diamine)$^{2+}$ Complexes

	Diamine		δ(^{13}C) for free amine^b		$\Delta\delta$(^{13}C) on diprotonation^c	$\Delta\delta$(^{13}C) on complexation^d [Pt(bpy)-(diamine)$^{2+}$]
en	NH$_2$CH$_2$CH$_2$NH	CH$_2$	44.6		−6.7	+3.7
pn	NH$_2$CHCH$_2$NH$_2$	CH	49.8		−3.1	+6.6
	CH$_3$	CH$_2$	49.4		−7.1	+3.5
		CH$_3$	21.2		−3.7	−4.1
cyda	(cyclohexane-1,2-diamine structure: γ, β, α — NH$_2$, NH$_2$)	α-CH	57.8		−4.5	+5.0
		β-CH$_2$	35.2		−4.8	−1.8
		γ-CH$_2$	26.4		−2.5	−1.3
N-Meen	CH$_3$NHCH$_2$CH$_2$NH	CH$_3$	36.9		−2.2	+4.8
		CH$_2$ (NH)	55.1		−8.3	+3.5
		CH$_2$ (NH$_2$)	41.9		−5.1	+2.3
N,N'-Me$_2$en	CH$_3$NHCH$_2$CH$_2$NHCH$_3$	CH$_3$	36.6		−1.8	+5.7 (trans) +6.8 (cis)
		CH$_2$	51.2		−5.6	+3.6 (trans) +5.3 (cis)
N,N-Me$_2$en	(CH$_3$)$_2$NCH$_2$CH$_2$NH$_2$	CH$_3$	46.1		−1.4	+7.0
		CH$_2$ (N)	62.6		−7.9	+8.8
		CH$_2$ (NH$_2$)	39.8		−4.3	+5.4

^{a} In ppm vs. external TMS; measured vs. internal dioxane. ^{b} Chemical shift of aqueous amine at pH >13. ^{c} Change in ^{13}C chemical shift (in ppm) for amine in aqueous solution at pH <2 vs. pH >13; negative protonation shifts are upfield. ^{d} Change in ^{13}C shift (in ppm) of free amine on chelation to platinum; positive shift is downfield.

attached to the observed carbon atom, and (3) the number of carbon substituents present on directly bound (α) carbon or nitrogen atoms. The effect of platinum chelation on amine carbon shifts is summarized in Table IV. In general, binding to the metal produces a 3–9-ppm downfield shift (vs. free aqueous amine) for any carbon nucleus α to a nitrogen donor atom; other carbon nuclei shift upfield with complexation. The effect on α carbons arises in part from electron withdrawal on covalent binding of the amine lone pair; however, changes in conformation on chelation may also be important. Table IV also includes a summary of amine protonation shifts which are generally found to be upfield. Such effects are not as yet well understood.

It is noteworthy that two features of the carbon shifts of the aliphatic diamine ring of the N^2,N^2-Me2pn complex stand out when compared with data for other N,N-dimethyl complexes. First, all N-methyl carbons for other N,N-dimethyl complexes are found to resonate in the range 52–54 ppm but in the N^2,N^2-Me2pn species one N-methyl carbon is shifted upfield to 45.71 ppm. At the same time the C-methyl resonance which occurs at 16–17 ppm in other pn type chelates is also found well upfield at 9.79 ppm. These upfield shifts probably result from the proximity of the N-methyl and C-methyl groups cis on the chelate ring as do the upfield steric shifts discussed earlier.[31,32] Such effects may be exceedingly useful for assignment purposes in future work with coordination complexes.

Registry No. Pt(bpy)(en)$^{2+}$, 24972-61-0; Pt(bpy)(pn)$^{2+}$, 56679-07-3; Pt(bpy)(ms-bn)$^{2+}$, 56679-08-4; Pt(bpy)(rac-bn)$^{2+}$, 56711-23-0; Pt(bpy)(C,C-Me2en)$^{2+}$, 56679-09-5; Pt(bpy)(C,C,C',C'-Me4en)$^{2+}$, 56679-10-8; Pt(bpy)(cyda)$^{2+}$, 56679-11-9; Pt(bpy)-(N-Meen)$^{2+}$, 24972-62-1; cis-Pt(bpy)(N,N'-Me2en)$^{2+}$, 56711-24-1; $trans$-Pt(bpy)(N,N'-Me2en)$^{2+}$, 56711-25-2; Pt(bpy)(N,N-Me2en)$^{2+}$, 24972-63-2; Pt(bpy)(N,N,N'-Me3en)$^{2+}$, 24972-65-4; Pt(bpy)(N^2,N^2-Me2pn)$^{2+}$, 56679-12-0; Pt(bpy)(N^1,N^1-Me2pn)$^{2+}$, 56679-13-1; Pt(bpy)(NH3)2^{2+}, 30051-91-3; Pt(bpy)(NH2CH3)2^{2+}, 56679-14-2; ^{13}C, 14762-74-4.

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are also found to possess opposite signs for interactions across two and three bonds. For example, α and β carbons of aliphatic amines bound to $Ni(acac)_2$[22] and $Gd(fod)_3$[23] show opposite signs for their contact shifts. Proton contact shifts behave similarly as seen in $Ni(NH_2CH_3)_6^{2+}$.[24]

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Structure of $(CH_3)_2AsCH_2CH_2CH_2As(CH_3)_2Mn(CO)_3GeCl_3$ in the Solid State and in Solution

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The reaction of $(CH_3)_2AsCH_2CH_2CH_2As(CH_3)_2Mn(CO)_3Cl$ with $GeCl_4$ affords *fac*-(L-L)Mn(CO)$_3$GeCl$_3$, **1**. The *mer* derivative is obtained from diphosMn(CO)$_3$Br. The structure of **1** in the solid state has been determined from three-dimensional X-ray counter data. The material crystallizes in space group $P2_1/n$ with four molecules in a monoclinic cell of dimensions $a = 8.215$ (3) Å, $b = 14.279$ (7) Å, $c = 16.787$ (8) Å, $\beta = 90.46$ (1)°, and $V = 1969.1$ Å^3. The structure was refined by full-matrix least-squares procedures to a conventional R factor of 8.3%. The structure of **1** consists of a slightly distorted octahedral geometry around the manganese with the chelate ring in a chair conformation such that the equatorial arsenic methyl groups are cis to the bulky GeCl$_3$ moiety. The chair is flattened about the As···As axis but is strongly puckered about the C···C axis. The ^{1}H NMR spectrum of **1**-d_2 in dichloromethane indicates that the ring is effectively locked in this solvent. The values of the $^3J_{HH}$ coupling constants indicate strong puckering of the chelate ring about the C···C axis although the derived As–C–C–C dihedral angle is less than the solid-state value.

Introduction

The conformations of six-membered chelate rings in metal complexes in solution have been of considerable interest in recent years.[2–8] In particular, using NMR techniques, it has been found that the complexes of the di(tertiary arsine) $(CH_3)_2AsCH_2CH_2CH_2As(CH_3)_2$ (L-L) of formula (L-L)-Mn(CO)$_3$X (X = Cl, Br, I) have their chelate rings locked in a chair conformation with the axial hydrogens on the two equivalent carbon atoms pointing toward the ligand X on the metal as indicated in A.[9] The corresponding (L-L)M(CO)$_4$
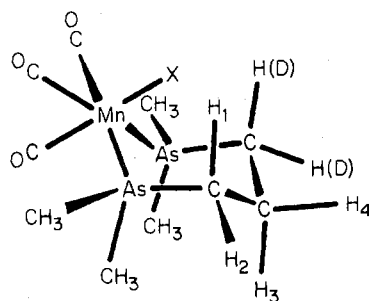
A

complexes undergo rapid chair ⇌ chair interconversion.[2a]

The locking of the ring in A is of interest because it seems that it arises because of repulsion between the ligand X on the metal and the arsenic methyl groups.[10] Interactions of this type are not found in rings usually studied by organic chemists so they are interesting in their own right. However it is worth noting that similar interactions could be present in the reaction intermediates of organic chemistry (replace the Mn(CO)$_3$X moiety in A with CR$_2$X); hence they could have an effect on reaction rates and reaction paths.

The present paper is part of a continuing study of the factors which affect chelate ring conformations.

Experimental Section

Hydrocarbon solvents were dried using CaH_2; CH_2Cl_2 was dried using P_2O_5. Infared spectra were recorded on a Perkin-Elmer 457 instrument using CO and polystyrene for calibration. NMR spectra were recorded on an extensively modified Varian HA 100 spectrometer; the ABCD spectrum was solved as previously described.[2] The compounds $[(CH_3)_2As(CH_2)_3As(CH_3)_2]Mn(CO)_3Cl$ and $[(CH_3)_2AsCD_2CH_2CH_2As(CH_3)_2]Mn(CO)_3Cl$ were prepared as previously;[2] diphosMn(CO)$_3$Br (diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) was prepared similarly. $GeCl_4$ was commercially available and used without further purification.

Preparation of $[(CH_3)_2As(CH_2)_3As(CH_3)_2]Mn(CO)_3GeCl_3$. A solution of (L-L)Mn(CO)$_3$Cl (0.436 g, 1 mmol) and GeCl$_4$ (0.75 ml) in benzene (10 ml) was heated at 150° in an evacuated sealed Carius tube for 55 hr. The tube was allowed to cool, and benzene and excess GeCl$_4$ were removed on the vacuum line. The residue was then sublimed at 100° (0.1 mm) to remove any (L-L)Mn(CO)$_3$Cl and L-L. The pure product was isolated by sublimation at 120° (0.1 mm) or recrystallized from CH_2Cl_2–*n*-heptane. It is essential to carry out the recrystallization under a nitrogen atmosphere with dry solvents. Crystals suitable for the X-ray crystallographic study were thus obtained. The yield of yellow $[(CH_3)_2As(CH_2)_3As(CH_3)_2]$-Mn(CO)$_3$GeCl$_3$ was approximately 65%. Anal. Calcd for $C_{10}H_{18}As_2Cl_3GeMnO_3$: C, 21.11; H, 3.00; Cl, 18.50. Found: C, 21.04; H, 3.18; Cl, 18.65. Infrared spectrum (CO region): 2025, 1968, 1946 cm^{-1} (cyclohexane solution); 2023, 1951 cm^{-1} (CH_2Cl_2 solution); all bands strong. ^{1}H NMR (CH_2Cl_2 solution): 1.74, 1.54 ppm (As–CH$_3$).

The deuterated analogue $(CH_3)_2AsCD_2CH_2CH_2As(CH_3)_2$-Mn(CO)$_3$GeCl$_3$ was prepared in a similar fashion.

Preparation of $[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]Mn(CO)_3GeCl_3$. An evacuated sealed Carius tube containing diphosMn(CO)$_3$Br (0.31 g, 0.5 mmol), GeCl$_4$ (1 ml), and benzene (10 ml) was heated at 160° for 7 days. The tube was then allowed to cool, and solvent and excess GeCl$_4$ were removed on the vacuum line.

The residue was extracted with two portions of warm CH_2Cl_2 (25 ml). The extracts were combined and evaporated to dryness to give crude diphosMn(CO)$_3$GeCl$_3$ (0.25 g, 66%). The analytical sample was recrystallized from CH_2Cl_2–*n*-heptane to give yellow crystals of