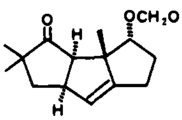

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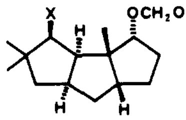
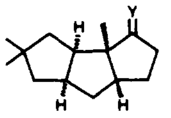
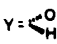


17 : X = OH

18 : X = $OCS_2CH_3$

19 : X = H



20 : Y = 
$\text{C}^{\text{OH}}_{\text{H}}$

21 : Y = O

tricyclic alcohol **17**[7] (oil, overall yield 87%). Assignment of the stereochemistry at C-3 and C-8 in **17** was based on a presumed attack by the reagents from the less hindered sides, and on the difficulty in forming a trans 5-5-fused ring,[13] in addition to the NMR spectrum. Deoxygenation of **17** using Barton's procedure,[14] which consisted of tri-*n*-butyltin hydride reduction of the corresponding *S*-methyl dithiocarbonate **18**,[7] gave the product **19**[7] (oil, yield 90%), which was deprotected (1% $H_2SO_4$ in aqueous acetone, 50 °C) to give the alcohol **20**[7] (oil) quantitatively. Oxidation of **20** with pyridinium chlorochromate in methylene chloride then gave the nor ketone **21**[7] (mp 44-45 °C, yield 86%). The spectral data (IR, NMR, and mass) were completely identical with those of an authentic sample[15] obtained from natural hirsutene. Since the nor ketone has been transformed into hirsutene,[3] the synthesis of **21** constitutes the completion of the task. Now that the utility of this unique skeletal rearrangement for a stereocontrolled synthesis of the hirsutane skeleton has been illustrated, the synthesis of highly oxidized coriolin-related substances is the subject of current studies.

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(7) All compounds gave satisfactory combustion analyses, IR, NMR and mass spectra consistent with the reported structures. Melting points were uncorrected. Unless otherwise noted, NMR ($\delta$, parts per million from $Me_4Si$) spectra were in $CDCl_3$ solution. Significant NMR spectral data are listed herein. **4**: 1.02, 1.08 (each s, Me), 2.08 (s, OAc). **6**: 0.87, 1.09, 1.16 (each s, Me), 2.01, 2.06 (each s, OAc), 5.01 (dt, $J_{5,6} = J_{6,7} = 10$, $J_{5',6} = 6$ Hz, H-6). 7: 0.91, 1.09, 1.24 (each s, Me), 2.01, 2.03 (each s, OAc), 5.25 (d, $J_{2,3} = 11$ Hz, H-3). **8**: 0.87, 1.15, 1.24 (each s, Me), 1.96, 2.03 (each s, OAc), 5.16 (dt, $J_{5,6} = J_{6,7} = 10$, $J_{5',6} = 6$ Hz, H-6). **10**: 0.88, 1.16, 1.26 (each s, Me), 1.99, 2.04 (each s, OAc), 5.15 (dt, $J_{5,6} = J_{6,7} = 10$, $J_{5',6} = 6$ Hz, H-6), 5.3 (m, H-11). **11**: 0.91, 1.12, 1.25 (each s, Me), 1.67, 2.03 (each s, OAc). **13**: 0.83, 1.07, 1.23 (each s, Me), 2.01 (d, $J_{2,7} = 14$ Hz, H-2), 2.44 (s, Me of Ts), 2.60 (dd, $J_{6,7} = 10$ Hz, H-7), 4.68 (dt, $J_{5,6} = 10$, $J_{5',6} = 5.5$ Hz, H-6). **14**: 0.96, 0.99, 1.10 (each s, Me), 1.44, 1.76 (each dd, $J_{5,5'} = 12.5$, $J_{5,6} = J_{5',6} = 9$ Hz, H-5 and -5′), 2.66 (ddt, $J_{2,6} = 11.5$, $J_{6,7} = 2.5$ Hz, H-6), 3.10 (d, H-2), 3.19 (d, H-7), 3.61 (d, $J_{10,11} = 5$, $J_{10',11} = 0$ Hz, H-11). 17: 0.97, 1.05, 1.18 (each s, Me), 3.58 (dd, $J_{2,3} = 9$, $J_{3,OH} = 3.5$ Hz, H-3, which, on adding 1 drop of $D_2O$, collapsed to a doublet), 3.82 (dd, $J_{10,11} = 7.5$, $J_{10',11} = 5$ Hz, H-11). **20**: 0.96, 0.98, 1.07 (each s, Me), 3.80 (m, H-11). **21** ($CCl_4$): 0.89, 0.94, 1.05 (each s, Me).

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(12) The IR spectrum showed the low-frequency shift of the carbonyl absorption (1715 $cm^{-1}$), supporting the strong hydrogen bonding between the C-3 carbonyl group and the C-11 hydroxyl group. This fact was also confirmed by the X-ray analysis.

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**Kuniaki Tatsuta,* Kohji Akimoto, Mitsuhiro Kinoshita**
*Department of Applied Chemistry, Keio University*
*Hiyoshi, Yokohama, Japan 223*

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## A Nuclear Magnetic Resonance Study of the Bis(2,2′-bipyridine)platinum(II) Cation in Basic Solution

*Sir:*

The reactions of nucleophiles with metal complexes containing phen and bpy[1] have recently collectively been attributed to attack on the ligand so that the chemistry of this important and large group of complexes has been relegated to what is essentially claimed to be the organic chemistry of the ligands.[2] For certain specific reactions involving octahedral complexes, this may be so. For four-coordinate complexes of Pt(II) and Pd(II) it has been challenged.[3]

The title complex (which because of steric hindrance is not strictly planar[3]) is known to react with base according to

$$[Pt(bpy)_2]^{2+} + OH^- \overset{K}{\rightleftarrows} [Pt(bpy)_2OH]^+ \qquad (1)$$

$$[Pt(bpy)_2OH]^+ + H_2O \xrightarrow{k} [Pt(bpy)(OH)(OH_2)]^+ + bpy \qquad (2)$$

$K = 10^{4.8}\ M^{-1}$ at 25 °C[3,4] so that a small excess of base gives a solution containing effectively only $[Pt(bpy)_2OH]^+$ which is long lived at room temperature; $t_{1/2} = 480$ h at 25 °C.[3] Gillard et al.[4] have presented $^1H$ NMR data for $[Pt(bpy)_2OH]^+$ in which new features at high field not present in $[Pt(bpy)_2]^{2+}$ were interpreted as demonstrating "nucleophilic attack (by $OH^-$) at the carbon atom adjacent to the ring nitrogen".[4] The quality of all of the spectra given by these authors[2] leaves much to be desired and we find their use for detailed interpretation unconvincing. We have therefore reinvestigated the $^1H$ NMR spectra and have also measured the corresponding $^{13}C$ NMR spectra.

Beer's law is obeyed for $[Pt(bpy)_2OH]^+$ over the whole concentration range and for all of the wavelengths investigated ($1 \times 10^{-6}$ to $4 \times 10^{-2}$ M, 240-480 nm). The spectra were independent of anion, $ClO_4^-$ or $NO_3^-$, and there were no absorption bands in the visible or the near-infrared region up to 1200 nm. We conclude therefore that polymerization is negligible.

From potentiometric titrations of $[Pt(bpy)_2]^{2+}$ with base we find that only *one* (1.02 ± 0.03) $OH^-$ is present in $[Pt(bpy)_2OH]^+$. $^{13}C$ and $^1H$ NMR spectra (for system of numbering, see Figure 1) in neutral solution are given in Figures 2 and 3. Both spectra show that all four aromatic rings are

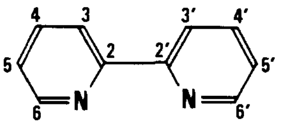

**Figure 1.** System of numbering.

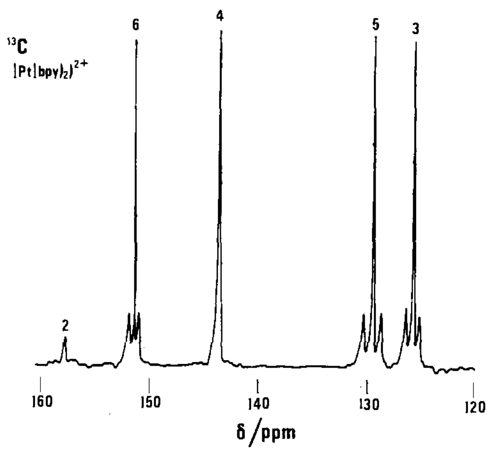

**Figure 2.** 22.63-MHz $^{13}$C NMR spectrum of $[Pt(bpy)_2](NO_3)_2$ ($C_{Pt(II)}$ = $3 \times 10^{-2}$ M) in 97% deuterated water at $T$ = 300 K. The spectrum was obtained on a Bruker WH-90 instrument in the Fourier transform mode (72.318 scans). The pulse width was 14 μs and the protons were decoupled using broad-band double irradiation. The chemical shift, $\delta$, was measured relative to dioxane (0.25%, $\delta_{dioxane}$ 67.40 ppm vs. $Me_4Si$). The assignment of the peaks was based on well-characterized $^{13}$C NMR spectra of heterocyclic compounds and was later confirmed by selective decoupling of the protons attached to the C atoms. The system of numbering is given in Figure 1. Spin-spin coupling is clearly demonstrated between $^{195}$Pt (33.8% abundance, $I = ^1/_2$) and C-3 ($^3J$ = 29 Hz), C-5 ($^3J$ = 36 Hz), and C-6 ($^2J$ = 28.5 Hz), while coupling to C-4 is barely noticeable ($^4J \leq 20$ Hz). Except for the reference peak, no other signals were observed in the range 0–200 ppm. All the protonated carbon atoms have equal intensities, within the experimental error of ±5%.

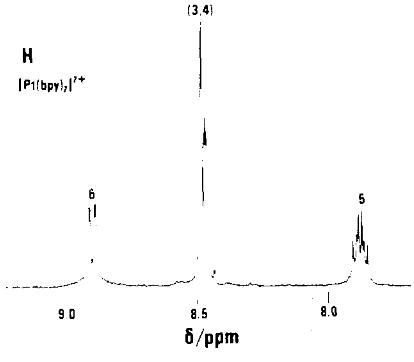

**Figure 3.** 270-MHz $^1$H NMR spectrum of $[Pt(bpy)_2](NO_3)_2$ ($C_{Pt(II)}$ = $4 \times 10^{-2}$ M) in 99.92% deuterated water at 300 K. The spectrum was obtained on a Bruker HX-270 instrument in the Fourier transform mode (50 scans) using a pulse width of 8 μs. The assignments were based on the spin multiplets and on experiments applying selective decoupling of the different groups. The system of numbering used here is given in Figure 1. The chemical shifts were measured relative to acetone (0.1%, $\delta_{acetone}$ 2.17 ppm vs. $Me_4Si$). Besides peaks shown here, no other signals were observed (with the exception of the acetone band and a small peak due to $H_2O$) in the range 0–10 ppm. The intensities of the three bands were 4.0:8.2:3.8 (±5%).

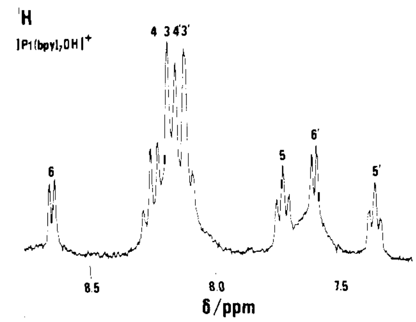

**Figure 4.** 270-MHz $^1$H NMR spectrum of $[Pt(bpy)_2](NO_3)_2$ in alkaline solution ($C_{Pt(II)}$ = $4 \times 10^{-2}$ M, $C_{OD^-}$ = $5 \times 10^{-2}$ M, $T$ = 300 K) using 99.92% deuterated water. The spectrum was obtained on a Bruker HX-270 instrument under the conditions given in Figure 3. The system of numbering applied here is in principle the same as used before, but the protons on one half of the bpy molecule have been marked with a prime in order to differentiate them from the protons on the other half, since the two aromatic rings of the ligand molecule are no longer identical. The different protons were identified by means of specific proton decoupling experiments which exhibited full self-consistency. $\delta$ is given in parts per million vs. $Me_4Si$ using the same reference as in Figure 3. No other peaks apart from those shown on this figure plus the reference and a small water signal were observed in the range 0–10 ppm. The intensities of the bands (from left to right) are 1.5:8.9:1.9:1.9:1.8 (±5%).

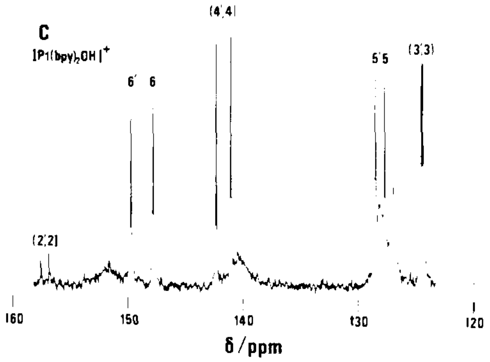

**Figure 5.** 67.89-MHz $^{13}$C NMR spectrum of $[Pt(bpy)_2](NO_3)_2$ in alkaline solution ($C_{Pt(II)}$ = $3 \times 10^{-2}$ M, $C_{OD^-}$ = $4 \times 10^{-2}$ M) in 97% deuterated water at 300 K. The spectrum was obtained on a Bruker HX-270 instrument in the Fourier transform mode (20.319 scans). The pulse width was 12 μs and the protons were decoupled using broad-band double irradiation. The chemical shifts were measured relative to dioxane using the same internal reference as in Figure 2. The same system of labeling the C atoms as was used for labeling the protons of Figure 4 is used here. In addition to the doubling of all lines, broad bands appear around δ 152 and 141 ppm with half-width ≃ 120 Hz and at 128 and 127 ppm with half-width ≃ 40 Hz. Except for the dioxane peak, no other signals than those shown here are seen in the range 0–200 ppm. It is seen that the platinum couplings have decreased below resolution. Because of the small chemical shift between H-3 and H-4, selective decoupling of these protons could not be performed accurately and, for this reason, it cannot be decided which of the C-3 and C-4 peaks belong to which H-3 or -3′ and H-4 or -4′ protons, respectively. All of the sharp peaks have equal intensities.

equivalent within the NMR time scale. We presume, by analogy to bis(2,2′-bipyridine)palladium(II) nitrate,[5] that the steric hindrance between the two ligands leads to "rectangular and tetrahedral" distortions.

The NMR spectra of solutions of $[Pt(bpy)_2OH]^+$ are more complex (Figures 4 and 5). In the $^{13}$C spectrum (Figure 5) the original five lines of Figure 2 are now double and still with equal intensity. Proton decoupling experiments were carried out and from these the fully consistent pictures given on Figures 4 and 5 emerged. Pairs of rings from the two ligands are equivalent. Since only 1 mol of $OH^-$ is consumed/mol of complex, this effectively rules out $OH^-$ attack of bpy ligands unless $OH^-$ exchange between two of the four aromatic rings is fast on the NMR time scale. This we consider unlikely.

Both $^1$H and $^{13}$C NMR spectra of $[Pt(bpy)_2OH]^+$ are very similar to the spectra of *cis*-bis(2,2′-bipyridine) complexes, exemplified by *cis*-$[Ir(bpy)_2Cl_2]^+$ and *cis*-$[Rh(bpy)_2Cl_2]^+$. The most characteristic feature of the $^1$H NMR spectra is that half of the H-6 hydrogens (labeled 6′) move upfield ($\delta_{H\text{-}6'}$ 7.6 ppm in the platinum complex and 7.8 ppm in the iridium complex[6]). In the latter complex this is because these hydrogens are directly above the plane of an aromatic ring and therefore more shielded. This is further substantiated by the

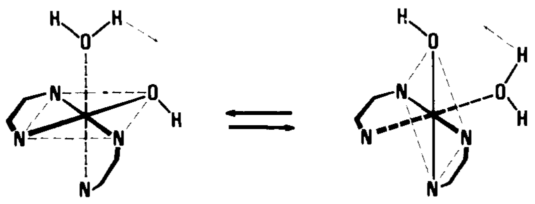

**Figure 6.** Proposed structure of title complex in basic solution.

$^{1}$H NMR spectrum of the tris(2,2′-bipyridine)osmium(II) complex[6] in which all of the H-6 hydrogens have δ 7.6 ppm. The $^{13}$C NMR spectra of [Pt(bpy)$_2$OH]$^+$ (Figure 5) and *cis*-[Rh(bpy)$_2$Cl$_2$]$^+$ (which was measured because it was readily available to us) are also very similar, and it is especially noteworthy that the four broad bands referred to in Figure 5 also appear in the kinetically inert rhodium complex. Since chemical exchange can presumably be excluded in this latter complex, these bands are probably due to intramolecular distortions in the flexible ligands.

All experimental evidence therefore points toward a configurational change from a distorted square planar structure in neutral solutions to a five- (or six-) coordinated species in alkaline solution. In the latter the two bpy ligands are in the cis position to each other. This is also supported by the $^{1}$H-methyl resonance in the platinum(II) complex with 5,5′-dimethyl-substituted bipyridine which splits in basic solution[4] just as do the H-5 and the H-5′ protons of Figure 4, and we see no way to explain our data within the "covalent hydration of the ligand" hypothesis advanced by Gillard.[2]

A more detailed structure of [Pt(bpy)$_2$OH]$^+$ must necessarily be speculative. This could be a five-coordinate trigonal bipyramid but also could be a distorted six-coordinate complex derived from a normal square planar Pt(II) complex. Thus the structure in Figure 6 is consistent with all the NMR experiments because proton transfer enables OH$^-$ to exchange between the two sites shown as OH and OH$_2$ in the figure with a rate which is rapid on the NMR time scale.

It is a notable feature of the so-called "Gillard pseudo base mechanism" that phen and bpy and also OH$^-$ and CN$^-$ are assumed to behave analogously. It is therefore relevant to the present work that OH$^-$ and CN$^-$ give analogous changes in the UV-visible spectrum of [Pt(phen)$_2$]$^{2+}$ and that studies of the [Pt(phen)$_2$CN]$^+$ cation have shown that the CN$^-$ group is directly coordinated to the platinum both in solution[7] and in the solid state.[8] Neither for this complex nor for [Pt(bpy)$_2$OH]$^+$ is it necessary to invoke new or "novel" mechanisms or structures.

The present NMR study confirms the suggestion[3] that the hydrolysis of Pt(bpy)$_2$$^{2+}$ in basic solution occurs via attack on the metal center and therefore by the associative mechanism generally accepted for substitution reactions in Pt(II) complexes.[9]

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## References and Notes

(1) The following abbreviations are used in this paper: phen, 1,10-phenanthroline; bpy, 2,2′-bipyridine.
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(10) To whom correspondence should be sent. Address until April 1981: The Weizmann Institute of Science, Department of Chemical Immunology, Rehovot, Israel.

**O. Farver,*[10] O. Mønsted, G. Nord**
*Chemistry AD (Inorganic and Physical Chemistry)*
*Royal Danish School of Pharmacy, and*
*Chemical Laboratory I (Inorganic Chemistry)*
*H. C. Ørsted Institute, University of Copenhagen*
*DK-2100 Copenhagen Ø, Denmark*

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## Stereoselective Aldol Condensations via Boron Enolates

*Sir:*

The aldol condensation is a reaction of fundamental importance in biosynthesis. Consequently, considerable effort has been expended to develop stereoregulated variants of this process in the laboratory. It is now well appreciated that *kinetic* aldol stereoselection is, in part, defined by enolate geometry for those condensations wherein two new stereocenters are created in the condensation step (Scheme I).[1,2] Given the reasonable postulate that the reaction proceeds via a pericyclic process,[1a,2a] the influence of variable steric parameters may be analyzed to determine their effects upon the relative heats of formation of diastereoisomeric transition states from an enolate of defined geometry. For example, for (*E*)-enolates one might anticipate that transition state T$_2$ might be destabilized relative to T$_1$ by maximizing *both* R$_2$ ↔ R$_1$ and R$_2$ ↔ L steric parameters. Heathcock and co-workers have recently dem-

Scheme I