$(1.4 \pm 0.2) \times 10^{-4}$ sec^{-1} at $11 \pm 3°$). The nmr spectrum had bands at δ 10.38 (1 H, m), 8.16 (1 H, d, $J = 3$), 3.9 (2 H, m), 3.8 (2 H, m), and 3.4 (3 H, m), which is comparable to that reported by Winstein for this ion.[14,15]

The use of 2-chlorobicyclo[2.1.1]hexane-2-d_1 as the reactant led at $-75°$ to a 1:1 mixture of 1-deuteriocyclohexenyl and 2-deuteriocyclohexenyl cations. At $-65°$, the deuterium begins to scramble about the cyclohexenyl ring. The ratio of the areas of the δ 10.18 and 8.22 bands changed from 3 to 2. Complete scrambling of the label was achieved after 6–10 hr at $-65°$.

(14) Dr. Philip Warner, private communication.
(15) The cyclohexenyl cation to methylcyclopentenyl cation has received considerable study in alkyl substituted cases: N. C. Deno and J. J. Houser, J. Amer. Chem. Soc., 86, 1741 (1964); N. C. Deno and R. R. Lastomirsky, ibid., 90, 4085 (1968); T. Sorensen, ibid., 89, 3782, 3794 (1967); 91, 6398 (1969); T. Sorensen and K. Ranganayakulu, ibid., 92, 6539 (1970).

Gunther Seybold, Pierre Vogel
Martin Saunders, Kenneth B. Wiberg*

Department of Chemistry, Yale University
New Haven, Connecticut 06520

Use of $^1|J_{^{195}Pt-^{15}N}|$ as a Probe into the Electronic Structure of Some Platinum(II)–Amine Complexes

Sir:

The question of the extent of π bonding in square-planar platinum(II) complexes remains a subject for considerable debate. Although the concept of "back-bonding" between platinum 5d orbitals and suitable ligand orbitals has frequently been invoked to explain most static and dynamic phenomena in transition metal chemistry including the kinetic trans effect[1] and certain infrared[2] and bond-length data,[3] the data obtained to date have failed to give an unambiguous answer to this problem.

Among the π interactions most frequently postulated are those between phosphorus 3d orbitals and metal d orbitals. Of particular interest in this context have been the efforts to correlate $^1|J_{^{195}Pt-^{31}P}|$ coupling constants with the extent of π-bond formation between these two nuclei.[4-6] From such data, Pidcock, et al.,[6] concluded that the very large differences in coupling constants between cis and trans platinum(II) complexes were due to differences in s character of the hybrids used by the platinum atom to form bonds to the phosphorus atom. These conclusions are supported by extended Huckel MO calculations.[7] The question at issue here is whether or not such changes occur as a consequence of the formation of d_π–d_π bonds. Thus, it seemed desirable to establish the extent of rehybridization accompanying cis–trans isomerization in systems

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in which the donor–acceptor bond does not have a significant π component.

In an effort to obtain an answer to this question, we have measured the ^{15}N nmr spectra of some complexes of platinum(II) with n-dodecylamine (A) labeled with >95 atom % ^{15}N ($I = \frac{1}{2}$). It was thought that a study of the changes in $^1|J_{^{195}Pt-^{15}N}|$ for a variety of platinum-amine complexes, relative to some phosphine analogs, might prove revealing. The choice of the amine as well as the degree of enrichment were dictated by the need for relatively high concentrations of ^{15}N.[8] The observed $^1|J_{^{195}Pt-^{15}N}|$ coupling constants are shown in Table I.

Table I. $^1|J_{^{195}Pt-^{15}N}|$ Coupling Constants in Some Platinum Complexes of n-Dodecylamine (A)

No.	Compound	J^a	J_{cis}/J_{trans}
1	cis-[PtCl$_2$A$_2$]	351	
2	trans-[PtCl$_2$A$_2$]	290	1.21
3	cis-[PtBr$_2$A$_2$]	334	
4	trans-[PtBr$_2$A$_2$]	279	1.20
5	cis-[PtCl$_4$A$_2$]	249	
6	cis-[PtBr$_4$A$_2$]	223	
7	[PtBrA$_5$]Br	342^b	
		288^c	1.19
8	[PtA$_4$]Br$_2$	298	

^{a} Measured as saturated solutions in chloroform. The data are estimated to be correct to ± 2 Hz. ^{b} For the nitrogen atom in a trans position to bromine. ^{c} For the nitrogen atoms in trans positions to each other.

The data can be interpreted in terms of the theory developed by Ramsay[9] which assumes the dominance of the Fermi contribution. Using the equation of Pople and Santry[10] for the directly bonded X–Y coupling in a covalent bond, one can write the expression for the term $^1|J_{^{195}Pt-^{15}N}|$ in an abbreviated form as

$$^1|J_{^{195}Pt-^{15}N}| \propto (\Delta E)^{-1} \alpha_{Pt}{}^2 \alpha_N{}^2 |\psi_{Pt(6s)}(0)|^2 |\psi_{N(2s)}(0)|^2$$

where ΔE is an average excitation energy, $\alpha_X{}^2$ is the s character of the hybrid used by X in the platinum-nitrogen bond, and $|\psi_a(0)|^2$ is the electron density of orbital a evaluated at the nucleus. As found for the phosphorus complexes examined earlier,[6] there is no correlation between the Pt–N coupling constants and the parameter ΔE.[11] Thus, it appears that the coupling is directly proportional to terms involving the s character of the bonding orbitals. A similar approach has been suggested for ^{15}N and has been shown to be valid for the ^{15}N–H bond in a series of aniline derivatives.[12] Such correlations have also been suggested[13] for other nuclei, e.g., the $^1|J_{^{195}Pt-^{13}C}|$ is responsive in a predictable manner to the s character of the carbon atom. In this

(8) $I = \frac{1}{2}$, natural abundance = 0.36%. The more abundant isotope ($I = 1$, natural abundance = 99.64%) possesses a quadrupole moment which frequently prohibits accurate measurements of the desired spin–spin interactions.
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(11) This is based on the assumption that the lowest energy electronic transitions are primary in determining the magnitude of ΔE and on the observation that such transitions show a trend which is opposite to that of the observed coupling constants.
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context it is also interesting to note that the ratio $J_{Pt(II)}/J_{Pt(IV)}$ (see Table I) is found to be 1.41 between compounds 1 and 5 and 1.50 between compounds 3 and 6, values which compare very favorably with the ratio calculated on the basis of a change of hybridization from dsp^2 to d^2sp^3 and with that of ca. 1.5 obtained for some related phosphine complexes.[6] The major influence of changes in s character on coupling constants does not appear to be restricted to those arising from directly bonded atoms as it is also found that the values of $^3|J_{195Pt-N-C-H}|$ in complexes [Pt(en)₂]Cl₂ and [PtCl₂-(en)₂]Cl₂ give a ratio of $J_{Pt(II)}/J_{Pt(IV)}$ of 1.60.[14]

As found previously in complexes cis- and trans-[PtX₂(R₃P)₂], the J_{Pt-N} values for complexes cis-[PtX₂A₂] are larger than those found for the corresponding trans complexes (see Table I), although in the former case $J_{Pt(II)}/J_{Pt(IV)}$ is ca. 1.5 and in the latter case, it is ca. 1.2. Thus, as found in the case of the phosphine complexes, *isomerization in complexes [PtX₂A₂] is accompanied by a significant amount of rehybridization which can only be due to σ effects.* On the other hand, because of the nature of the equations used to express $^1|J_{195Pt-16N}|$ and $^1|J_{195Pt-31P}|$ the difference in cis/trans ratios between amine and phosphine complexes cannot be taken as an indication that rehybridization occurs to a different extent in the complexes of the two ligands.

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Paul S. Pregosin, H. Omura, L. M. Venanzi*
Department of Chemistry, University of Delaware
Newark, Delaware 19711
Received August 12, 1972

Syntheses of Ferrous–Porphyrin Complexes. A Hypothetical Model for Deoxymyoglobin

Sir:

Intense, sustained interest in simple models for oxy- and deoxymyoglobin and hemoglobin has resulted in many reports concerned with iron porphyrins. However, few of these describe experimentally well characterized iron(II) porphyrins. Only low-spin complexes of the type Fe(porphyrin)L₂ for L = pyridine[1,2] and piperidine[3] appear to be well documented, and the crystal structure of Fe(TPP)(piperidine)₂ (TPP = meso-tetraphenylporphyrin) has been determined.[4] Herein we describe a clean high-yield preparation of unsubstituted Fe(TPP) and the conversion of this isolated complex into a series of Fe(II)–TPP derivatives including a five-coordinate high-spin complex which appears to be a model for deoxymyoglobin.

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Reduction of FeCl(TPP) with Cr(acac)₂[5] in rigorously degassed benzene, followed by precipitation with ethanol and recrystallization from benzene–ethanol (using Schlenk tube techniques within an inert atmosphere chamber), affords an 80% yield of purple crystalline Fe(TPP) (1). *Anal.* Calcd for C₄₄H₂₈N₄Fe: C, 79.05; H, 4.2; N, 8.4; Fe, 8.4. Found: C, 79.0; H, 4.45; N, 8.65; Fe, 8.4. The postulated four-coordinate nature of 1 cannot be verified without a crystallographic study or a molecular weight determination and so far our measurement of the latter has been frustrated by its meager solubility and extreme solution air sensitivity. Four-coordinate d^6 complexes are rare and none have been characterized by X-ray crystallographic analysis. Phthalocyanineiron(II)—a good model for 1—has an unusual magnetic moment (μ = 3.71 BM at 25°) and has been extensively studied.[6] The moment observed for 1 (μ = 4.4 BM at 25°)[7] is intermediate between that expected for high- and low-spin Fe(II). It should be noted that most four-coordinate iron complexes are tetrahedral so that the constrictions imposed by the essentially planar porphyrin may force an unusual electronic state upon the iron in 1. Conversely the iron(II) may tend to maximize distortion from planarity of the porphyrin making the crystallographic analysis of 1 a paramount objective.

As expected Fe(TPP) reacts rapidly with strong field nitrogen donors L, affording diamagnetic low-spin complexes Fe(TPP)L₂ (L = imidazole, pyridine, piperidine).[7] Tetrahydrofuran (THF) affords the high-spin complex FeTPP(THF)₂, μ = 5.1 BM at 25°. *Anal.* Calcd for C₅₂H₄₄N₄O₂Fe: C, 76.85; H, 5.45; N, 6.9; Fe, 6.9. Found: C, 76.7; H, 5.6; N, 7.2; Fe, 7.0. While this work was in progress a different preparation of Fe(TPP) and Fe(TPP)(THF)₂ was published,[2] but elemental analyses were poor and the reported magnetic moments differ from this work.

X-Ray diffraction studies of myoglobin (Mb)[8] and hemoglobin (Hb)[9] and predictions advanced by Hoard[10] suggest the high-spin deoxy–heme geometry to be five-coordinate square pyramidal with the iron atom displaced 0.5–0.8 Å above the porphyrin plane toward the axial histidyl imidazole. In all low-spin six-coordinate complexes such as Fe(TPP)(piperidine)₂[4] and probably oxyhemoglobin,[11] the iron is thought to occupy an in-plane position.

The absence of simple models for deoxymyoglobin undoubtedly results from the affinity of five-coordinate iron(II) to bind another imidazole forming low-spin six-coordinate complexes. In the natural system the shape of the globin protein pocket enforces five-coordination. Using a simple concept of nonbonded steric inter-

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