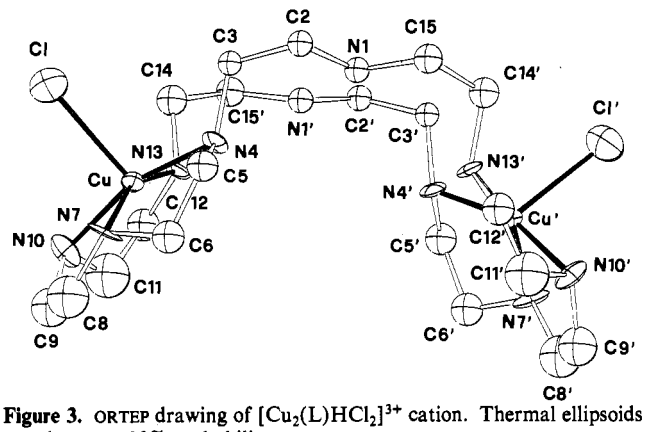

Figure 3. ORTEP drawing of $[Cu_2(L)HCl_2]^{3+}$ cation. Thermal ellipsoids are shown at 30% probability.

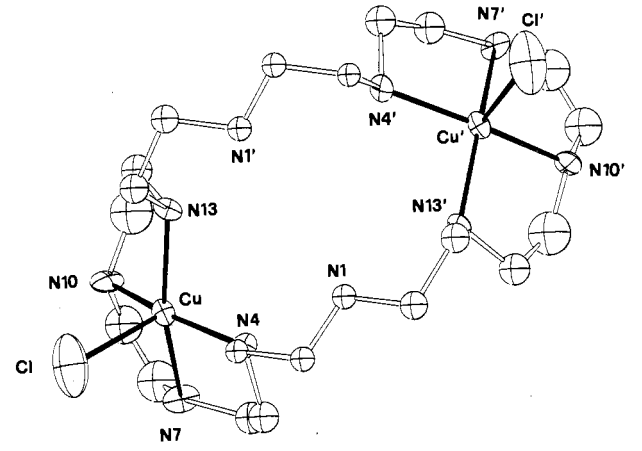

Figure 4. Top view of $[Cu_2(L)HCl_2]^{3+}$ cation. Thermal ellipsoids are shown at 30% probability.

forming a slightly distorted square pyramid (Figure 3). The site of protonation must be on the N(1) or N(1′) atom of the macrocycle, but owing to the presence of the twofold axis, the two nitrogen atoms are crystallographically equivalent and therefore the proton is statistically distributed between them. The distance of 3.90 (3) Å between N(1) and N(1′) (Figure 4) rules out any possibility of bridging for the hydrogen atom. The nitrogen atoms lie in the basal plane with a maximum deviation of 0.05 Å from the least-squares plane through them. The copper atom is 0.34 Å out of the plane. Bond lengths and angles of the binuclear complex are reported in Table V. The mean Cu–N distance of 2.03 (2) Å is identical (within experimental error) with the analogous distance in the $[Cu_2(bistrien)Cl_2](ClO_4)_2$ complex[3] whereas the Cu–Cl distance (2.43 (1) Å) is shorter than the Cu–Cl bond length found in the same complex (2.48 (1) Å), in which the copper atom interacts with a further chloride ion at 3.31 Å. The intramolecular Cu–Cu distance is 7.26 (1) Å compared to 6.138 (1) Å found in $[Cu_2(bistrien)Cl_2](ClO_4)_2$. The macrocycle has a saddle-shaped configuration; the two least-squares planes through the coordinating nitrogens form an angle of 83.8° (see supplementary material). As in the $[Cu_2(bistrien)Cl_2](ClO_4)_2$ compound, all the five-membered chelate rings are in the gauche configuration.

It should be noticed that crystal structures of protonated macrocyclic complexes are rare because protonated species are present as a small fraction and in a narrow pH range in the solution equilibria. In spite of the above considerations, a protonated complex species $[Cu_2(L)H]Cl_2(ClO_4)_3 \cdot 4H_2O$ crystallized in which one of the uncoordinated atoms is protonated. The occurrence of such monoprotonated species in the solid state can be attributed to various stabilizing effects such as chloride coordination and a hydrogen-bonding network. In solution the binuclear complex $[Cu_2(L)]^{4+}$ seems to behave differently because as previously mentioned, the thermodynamic data suggest that a Cu–N bond is broken each time a proton is added to form $[Cu_2(L)H]^{5+}$, $[Cu_2(L)H_2]^{6+}$, and $[Cu_2(L)H_3]^{7+}$ species.

Acknowledgment. We thank Dr. S. Seniori Costantini for microanalyses and M. Poggiali and R. Tarducci for technical help. We thank also the ISSECC, Florence (CNR), for the use of their diffractometer. Financial support from the Progetto Chimica Fine e Secondaria of the Italian Research Council (CNR) is gratefully acknowledged.

Registry No. **a**, 112-57-2; **b**, 99142-42-4; **c**, 107010-90-2; **d**, 107035-78-9; **f**, 107010-91-3; L, 107010-92-4; TsCl, 98-59-9; MsCl, 124-63-0; $[Cu_2(L)HCl_2](ClO_4)_3 \cdot 4H_2O$, 107010-95-7; $[Cu_2(L)]^{4+}$, 107010-96-8; ethylene carbonate, 96-49-1.

Supplementary Material Available: Tables of thermal parameters, complete bond lengths and angles, hydrogen bonds, and least-squares-plane equations (4 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Protonation of Six-Coordinate Hydrido Complexes of Osmium(II). Examples of Seven-Coordination in Osmium Polypyridyl Chemistry

B. Patrick Sullivan,* Richard S. Lumpkin, and Thomas J. Meyer*

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The hydrido–osmium(II) complexes *trans*-$[Os(chelate)(PPh_3)_2(CO)H](PF_6)$ (chelate = 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, and 5,5′-dimethyl-2,2′-bipyridine) undergo protonation with trifluoromethanesulfonic acid (TFMSH) in CH_2Cl_2 or trifluoroacetic acid (TFAH) media to form the dihydrido complexes $[Os(chelate)(PPh_3)_2(CO)H_2]^{2+}$. Through the interpretation of a series of NMR spectral experiments involving ^1H, ^2H, and ^{31}P nuclei, arguments are developed that implicate a pentagonal-bipyramidal solution structure for $[Os(bpy)(PPh_3)_2(CO)H_2]^{2+}$ in 10% TFMSH–90% TFAH (by volume) solution. The proposed structure, which has PPh_3 ligands above and below the pentagonal plane but adjacent hydrido ligands, is consistent with a protonation mechanism involving the least molecular reorganization on going from octahedral *trans*-$[Os(bpy)(PPh_3)_2(CO)H]^+$ to pentagonal-bipyramidal $[Os(bpy)(PPh_3)_2(CO)H_2]^{2+}$.

Trifluoromethanesulfonate (TFMS; $CF_3SO_3^-$) complexes of the transition metals are often of preparative value as intermediates in net substitution reactions. The use of the TFMS ligand as a leaving group has been the theme of a series of kinetic[1] and

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synthetic studies[2,3] which have convincingly demonstrated the utility of the ligand as a synthetic tool for developing the coordination chemistry of the relatively inert second- and third-row transition metals.

Two general and convenient preparative routes to metal–TFMS compounds are shown in eq 1 and 2 (bpy = 2,2′-bipyridine). The

$$[Os(bpy)_2(CO)Cl]^+ + TFMSH \xrightarrow{\Delta} [Os(bpy)_2(CO)(TFMS)]^+ + HCl \quad (1)$$

$$[Os(bpy)_2(CO)H]^+ + TFMSH \xrightarrow[CH_2Cl_2]{25\ ^\circ C} [Os(bpy)_2(CO)(TFMS)]^+ + H_2 \quad (2)$$

net chemistry involves the acid-induced loss of hydride as H_2 or of chloride as HCl concomitant with the incorporation of the potentially labile trifluoromethanesulfonate ligand into the metal coordination sphere.[2c]

An intriguing mechanistic point associated with both reactions 1 and 2 is the possibility that a proton initially adds at the metal center to give a seven-coordinate intermediate. During an investigation[2c] of the chemistry of polypyridyl hydrido complexes of Os(II) we noted that the complex *trans*-$[Os(bpy)(PPh_3)_2(CO)H]PF_6$ appeared to undergo a reversible reaction with TFMSH to produce an intermediate that is stable with respect to the evolution of H_2. In this paper we describe the evidence that we have obtained concerning the formation and structure in solution of the protonated species $[Os(bpy)(PPh_3)_2(CO)H_2]^{2+}$.

Experimental Section

Materials. All solvents were of reagent grade and used as received. Deuteriated solvents of spectroscopic grade were obtained from Aldrich Chemical Co. and were used without further purification.

***mer*-$[Os(PPh_3)_3(CO)(H)Cl]$.** The complex was prepared by using the method of Ahmad, Robinson, and Uttley[4] with $[N(n\text{-}C_4H_9)_4]_2OsCl_6$ as the osmium precursor.

***trans*-$[Os(bpy)(PPh_3)_2(CO)H](PF_6)$.** The PF_6^- salt of the hydrido complex was prepared and purified by a modification of the method previously reported by us.[2d] The preparation was accomplished by heating at reflux equimolar amounts of $[Os(PPh_3)_3(CO)(H)Cl]$ and 2,2′-bipyridine (~0.5 mmol, Aldrich) in 20 mL of ethylene glycol for 10 min, at which time the solution turned yellow. After the solution was cooled to room temperature, the cation was precipitated by the addition of ~20 mL of saturated aqueous KPF_6. The yellow flocculent precipitate was collected and purified by chromatography on alumina using a 1:1 acetonitrile–toluene solution as the eluent. Two bands were observed; the first yellow band was collected, the solution evaporated, and the solid reprecipitated from acetonitrile by the addition of ether. A pink band remained at the top of the column and was not collected.

Substituted-Bipyridyl Derivatives. Salts of the type *trans*-$[Os(chelate)(PPh_3)_2(CO)H](PF_6)$ (where chelate = 4,4′-dimethyl-2,2′-bipyridine, 5,5′-dimethyl-2,2′-bipyridine, and 2,2′-bipyridine-d_8) were prepared by the same procedure used above for the preparation of *trans*-$[Os(bpy)(PPh_3)_2(CO)H](PF_6)$. All of these complexes were purified by recrystallization from methylene chloride by the slow addition of ether.

$[Os(chelate)(PPh_3)_2(CO)H]^{2+}$. Complexes of the type $[Os(chelate)(PPh_3)_2(CO)H]^{2+}$ (where chelate = 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 5,5′-dimethyl-2,2′-bipyridine, and 2,2′-bipyridine-d_8) were prepared by the addition of anhydrous trifluoromethanesulfonic acid to a solution of $[Os(chelate)(PPh_3)_2(CO)H](PF_6)$ in a dry, noncoordinating solvent such as methylene chloride or trifluoroacetic acid (TFAH; CF_3CO_2H). The resultant solutions varied from 10 to 50% by volume in TFMSH. Upon addition of the acid the solution changed from a dark yellow to a pale, clear yellow. Upon addition of ether, wet ether, or water to the acidified solution, the starting salt *trans*-$[Os(chelate)(PPh_3)_2(CO)H](PF_6)$ was regenerated quantitatively as shown by isolation and weighing after drying and spectral analysis.

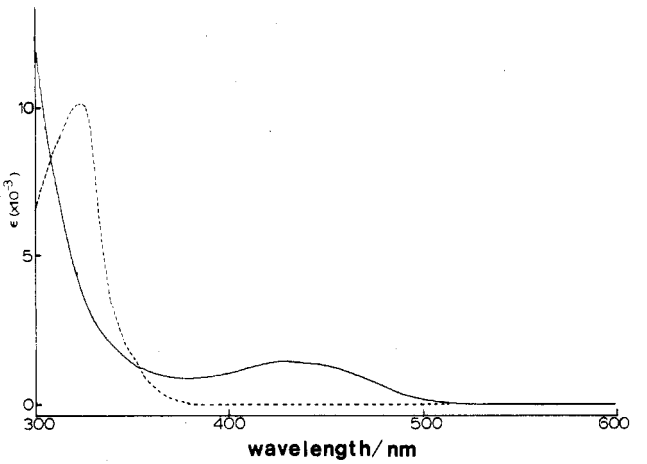


Figure 1. UV–visible spectra of *trans*-$[Os(bpy)(PPh_3)_2(CO)H](PF_6)$ in neat trifluoroacetic acid (solid line) and in 10% trifluoromethanesulfonic acid–90% trifluoroacetic acid (by volume) (dashed line).

Visible Spectra. The visible spectra of *trans*-$[Os(bpy)(PPh_3)_2(CO)H]^+$ and $[Os(bpy)(PPh_3)_2(CO)H_2]^{2+}$ are shown in Figure 1. The spectra were obtained in trifluoroacetic acid with various amounts of trifluoromethanesulfonic acid added in order to obtain the spectrum of the dihydride. The spectrum of the dihydride did not change when the composition of the solution was increased up to 50% v:v in TFMSH.

NMR Spectral Data. ^1H, ^2H, and ^{31}P NMR spectral data were recorded on a Bruker 250-MHz instrument. Proton spectra were taken in acetonitrile-d_3 with Me_4Si as the internal standard for the parent compounds, *trans*-$[Os(chelate)(PPh_3)_2(CO)H]^+$. For the NMR spectral experiments that involved the use of trifluoroacetic acid–trifluoromethanesulfonic acid mixtures, an external standard and lock (CD_3CN–Me_4Si mixture) was employed. All of the dihydride samples were prepared in an inert-atmosphere drybox (Vacuum Atmospheres) to keep the samples free of water. ^{31}P NMR spectra were obtained in the same solvent systems, acetonitrile-d_3 for the parent species and TFMSH–TFAH mixtures for the dihydride. Low-temperature ^{31}P spectra were taken at −5 °C, near the freezing point of trifluoroacetic acid (−15 °C), and in this case H_3PO_4 was used as the external standard.

Results and Discussion

In a previous study of polypyridyl hydrido–carbonyl complexes of Os(II), a relatively high-yield synthetic route to complexes of the type *trans*-$[Os(chelate)(PPh_3)_2(CO)H]^+$ was described, where chelate was any of a variety of polypyridyl ligands such as 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or their derivatives.[2c] The method as shown in eq 3 relied upon the very reactive precursor $Os(PPh_3)_3(CO)HCl$ and resulted in >90% conversion to the yellow hydrido–carbonyl complexes.

$$[Os(PPh_3)_3(CO)HCl] + chelate \xrightarrow[HOCH_2CH_2OMe]{\Delta} trans\text{-}[Os(chelate)(PPh_3)_2(CO)H]^+ + PPh_3 + Cl^- \quad (3)$$

The formal Os(IV) dihydrido complexes, which are the focus of this paper, resulted from the treatment of the resulting complex *trans*-$[Os(bpy)(PPh_3)_2(CO)H]^+$ with TFMSH in CH_2Cl_2 solution at room temperature. Instead of formation of the potentially useful synthetic intermediate *trans*-$[Os(bpy)(PPh_3)_2(CO)(TFMS)]^+$ by elimination of H_2 and capture by the TFMS anion, an insoluble, colorless oil appeared with no gas evolution. Addition of anhydrous Et_2O or Et_2O–H_2O mixtures to the reaction mixture gave back the starting hydrido–carbonyl complex quantitatively.

This observation was particularly intriguing since, for other d^6 mixed hydrido–polypyridine complexes based on Re, Os, Ru, or Ir, relatively rapid reactions had been observed between the complexes and TFMSH in noncoordinating solvents to give the corresponding TFMS complex.[2c,d]

After several unsuccessful attempts to find a suitable solvent for characterizing the protonated complex spectroscopically, CF_3COOH (TFAH) was chosen since it was most compatible with the ^1H NMR spectral experiments to be discussed below.

(1) Dixon, N. E.; Lawrence, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 847.
(2) (a) Buckingham, D. A.; Creswell, P. J.; Sargeson, A. M.; Jackson, W. G. *Inorg. Chem.* **1981**, *20*, 1647. (b) Lay, P. A.; Magnuson, R. H.; Sen. J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658. (c) Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Organometallics* **1984**, *3*, 1241. (d) Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1984**, 403.
(3) Drew, M. G. *B. Prog. Inorg. Chem.* **1977**, *23*, 67.
(4) Ahmad, N.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc.* **1972**, 843.

Table I. Absorption Spectrum of *trans*-$[Os(bpy)(PPh_3)_2(CO)H](PF_6)$ in Polar Organic and Acidic Solutions

solvent	abs band energies, nm	ϵ_{max}
CH_3CN	417	1670
	298	15700
1,2-Cl_2-C_6H_4	438	*a*
CF_3COOH	435 (bd)	1510
	321	4520
10% TFMSH in	~345 (sh)	1380
CF_3COOH	321	10200
50% TFMSH in	~343 (sh)	1610
CF_3COOH	321	10000

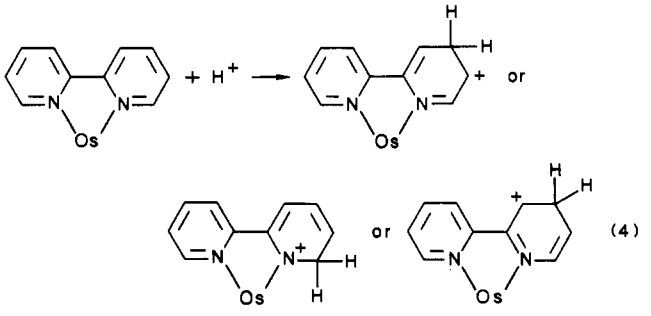
[a] Not recorded.

Electronic Spectra of *trans*-$[Os(bpy)(PPh_3)_2(CO)H]^+$ in Acidic Solution. As shown in Figure 1, the electronic spectrum of *trans*-$[Os(bpy)(PPh_3)_2(CO)H]^+$ in the region 300–600 nm, in CF_3COOH, has two main regions of absorption. The low-energy feature is due to a manifold of metal-to-ligand charge-transfer (MLCT) transitions exhibiting a maximum at 435 nm.[2e,5] This value compares well with the value of 438 nm obtained in 1,2-dichlorobenzene solution (see Table I). The high-energy end of the spectrum is dominated by intense ligand (PPh_3 and bpy)-localized, $\pi-\pi^*$ transitions as has been found in other mixed bpy–arylphosphine metal complexes.[6]

In Table I are summarized the absorption spectral properties of the complex in 10% TFMSH–90% TFAH and 50% TFMSH–50% TFAH and, for further comparison, in CH_3CN and 1,2-dichlorobenzene. It is apparent from the data shown in Figure 1 and in Table I that addition of 10% TFMSH causes a dramatic change in the electronic spectrum as manifested by the appearance of one intense transition at 321 nm and a discernable shoulder at about 345 nm. The peak positions and extinction coefficients in 50% TFMSH are the same within experimental error as in 10% TFMSH, showing that protonation is complete.

Reasonable protonation sites in the molecule that could cause significant electronic spectral changes are the carbonyl oxygen, the bpy ligand, and the metal center. The shift of the MLCT band at λ_{max} = 435 nm to a shoulder at 345 nm and the red shift in $\pi-\pi^*$(bpy) from 290 to 321 nm are most consistent with metal protonation. Protonation at Os(II) would create an electron-deficient metal site with considerably stabilized $d\pi$ levels and lead to an increase in the MLCT transition energy in the protonated complex. When the formal charge at the Os center is increased, the $\pi-\pi^*$ transition energies are expected to red shift.[7]

Protonation of CO either at C or O would also be expected to increase the MLCT absorption band energy through stabilization of the $d\pi$ levels by enhanced back-bonding. On the other hand, protonation at the bpy ligand to give an electron-deficient, carbocationic center on the ligand (eq 4) should shift the MLCT band



to lower energy.

The NMR spectral results below clearly support protonation at the metal.

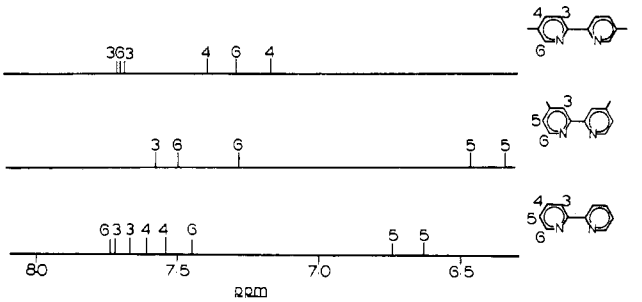
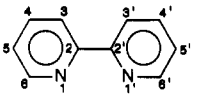


Figure 2. Correlation diagram of ^1H NMR spectral shifts for $[Os(chelate)(PPh_3)_2H]^+$ (where chelate = bpy and the dimethyl derivatives 4,4′-Me_2bpy and 5,5′-Me_2bpy). The "sticks" in each diagram refer to the center of the multiplet, and the assignment of the resonance is shown above each "stick".

Assignment of the ^1H NMR Spectrum of *trans*-$[Os(bpy)(PPh_3)_2(CO)H]^+$. In order to understand the NMR spectral properties of the parent complex before protonation, a series of derivatives were made which allowed general assignment of the ^1H NMR spectrum. The derivatives included *trans*-$[Os(Me_2chelate)(PPh_3)_2(CO)H]^+$ (where Me_2chelate = 4,4′-Me_2-2,2′-bpy and 5,5′-Me_2-2,2′-bpy) and the deuteriated complex *trans*-$[Os(bpy\text{-}d_8)(PPh_3)_2(CO)H]^+$.

The general features of the proton NMR spectrum of *trans*-$[Os(bpy)(PPh_3)_2(CO)H]^+$ consist of eight discernable bpy resonances, a narrow region of PPh_3 aromatic resonances, and a well-resolved triplet Os–H resonance at −12.2 ppm (vs. Me_4Si). By comparison of the shift and coupling patterns in the bpy resonance region for the dimethyl derivatives with those of the parent complex, assignments for all eight protons can be made. The assignments are presented in the form of a shift correlation diagram in Figure 2, where the numbering system used for the bpy ligand is shown as follows:



Inspection of the relative shift positions for the *trans*-$[Os(chelate)(PPh_3)_2(CO)H](PF_6)$ series shows that the 6,6′-proton pair is widely split (1.1 ppm), the 5,5′-pair is less so (0.7 ppm), and both the 4,4′- and the 3,3′-protons experience very similar chemical shifts in all three complexes. The 6,6′-protons usually resonate downfield from the other protons in mono(bipyridyl) complexes, so that the occurrence of one proton of the 6,6′-pair substantially upfield must be due to a large diamagnetic anisotropy within the molecule and, in particular, to a difference in electron distribution between the ligands cis to the 6- and 6′-positions of the bpy. The source of the anisotropy cannot be the trans-PPh_3 ligands because of their symmetrical disposition with regard to the polypyridine ligand. Molecular models reveal, however, that one proton of the 6,6′-pair points directly at the center of the carbonyl π cloud, which should cause an upfield shift relative to the shift for second proton, which is directed toward the hydride ligand. For the 5,5′-pair, one of the C–H bond pairs is roughly parallel with the CO group and should experience substantially less shielding. Both of the protons of the 4,4′- and 3,3′-pairs are directed well away from either the CO or H ligands and should experience similar magnetic environments.

For the methyl derivatives, as shown in Figure 2, several trends in the NMR spectral shift positions can be identified, which are of importance in establishing the solution structure of $[Os(bpy)(PPh_3)_2(CO)H_2]^{2+}$. As a first point, the average shift of the 6,6′-pair of protons moves upfield upon methyl substitution in the order bpy < 4,4′-Me_2bpy ≈ 5,5′-Me_2bpy and the magnitude of the change varies as the distance separating the electron-releasing methyl group and the proton site observed. A similar trend, although smaller in magnitude, exists for the 3,3′-pair, the upfield shift order being bpy < 5,5′-Me_2bpy < 4,4′-Me_2bpy. More direct effects arising from changes in electron density are also seen in that the 4,4′-protons move upfield upon substitution by methyl

(5) (a) Kober, E. M. Ph.D. Dissertation, The University of North Carolina, Chapel Hill, NC, 1981. (b) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1614.
(6) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
(7) Bryant, G. M.; Fergusson, J. E. *Aust. J. Chem.* **1971**, *24*, 275.

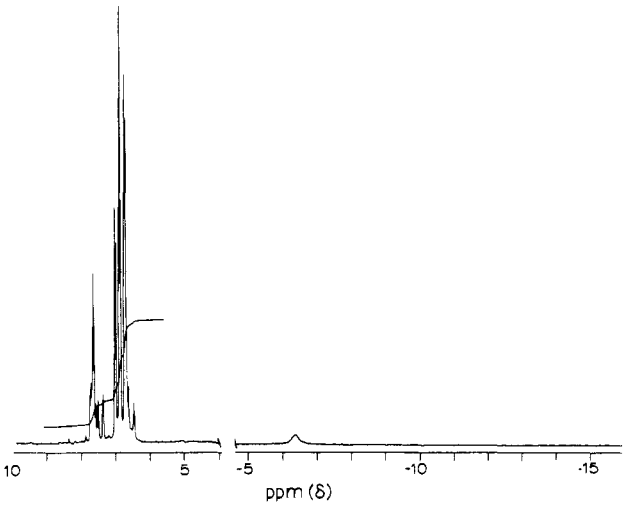


Figure 3. Proton NMR spectrum of *trans*-[Os(bpy)(PPh_3)$_2$(CO)H](PF_6) taken in 10% trifluoromethanesulfonic acid–90% trifluoroacetic acid (see text).

groups at the 5,5′-positions and the 5,5′-pair of protons moves upfield upon methyl substitution at the 4,4′-positions.

Effect of Trifluoromethanesulfonic Acid on the ^{1}H NMR Spectrum of *trans*-[Os(bpy)(PPh_3)$_2$(CO)H]$^+$. The ^{1}H NMR spectrum of *trans*-[Os(bpy)(PPh_3)$_2$(CO)H]$^+$ in trifluoroacetic acid at room temperature is very similar in the aromatic proton region to the spectrum of the complex in CD_3CN solution except that the metal hydride resonance has merged with the base line. The loss of the hydrido resonance can be interpreted as an exchange effect based on the equilibrium shown in eq 5, where in CF_3CO_2H the equilibrium lies well to the left and proton exchange is still rapid.

$$\textit{trans}\text{-[Os(bpy)(PPh}_3\text{)}_2\text{(CO)H]}^+ + CF_3COOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Os(bpy)(PPh_3)_2(CO)H_2]^{2+} + CF_3COO^- \quad (5)$$

Addition of TFMSH to a TFAH solution (10–50% by volume depending upon the experimental run) of the complex resulted in the dramatic change in the ^{1}H NMR spectrum that is shown in Figure 3. The most noticeable effects are the splitting of the PPh_3 resonances into distinct ortho, meta, and para components, a general narrowing of the shift differences between the bpy protons, and, most significantly, the appearance of a broadened signal at ca. –6.4 ppm, which integrates to 1.5 protons relative to the aromatic protons. As will be demonstrated below, the new resonance can be attributed to two new rapidly exchanging osmium hydride protons, i.e., the equilibrium shown in eq 5 now lies substantially to the right.[8]

Identification of the Site of Protonation. As pointed out earlier, it is conceivable that protonation of the complex could occur at CO, at bpy, at the phenyl groups, or at the metal. Protonation at aromatic carbon atoms would result in rapid hydrogen exchange; consequently, several labeling experiments were performed involving both *trans*-[Os(bpy)(PPh_3)$_2$(CO)H]$^+$ and its bpy-d_8 analogue. For the ^{2}H NMR spectrum of the bpy-d_8 complex in CH_3CN a 1:5:1:1 pattern was found, which is similar in relative shift positions to the proton NMR spectrum but less well-resolved due to the large linewidth of the ^{2}H signals. The spectrum of *trans*-[Os(bpy-d_8)(PPh_3)$_2$(CO)H]$^+$ in 10% TFMSH–90% TFAH solution is not very distinctive since it is apparent that all of the ^{2}H shifts have moved close together to yield only several groupings (essentially a 5:3 pattern) of resonances. Qualitatively, this is the same behavior observed in the ^{1}H NMR spectrum under the same conditions.

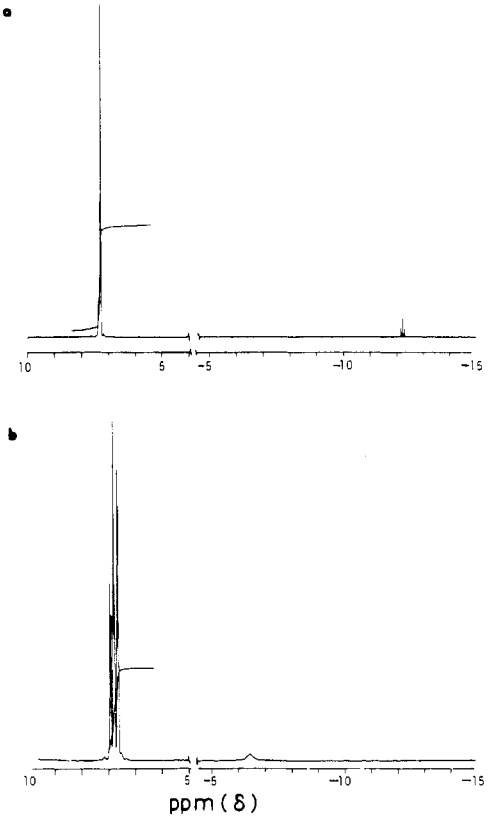


Figure 4. ^{1}H NMR spectra of *trans*-[Os(bpy-d_8)(PPh_3)$_2$(CO)H](PF_6) taken in (a) CD_3CN solution and (b) 10% trifluoromethanesulfonic acid –90% trifluoroacetic acid solution.

The ^{1}H NMR spectra of the bpy-d_8 complex in CD_3CN solution and in 10% TFMSH–90% TFAH are shown in parts a and b, respectively, of Figure 4. For the spectrum taken in CD_3CN solution, only the phenyl aromatic region and the characteristic Os–H triplet is apparent, while for the spectrum in acidic medium the split aromatic region and the new broadened upfield resonance at –6.4 ppm are both observed. In a separate experiment the bpy-d_8 sample was isolated from the acid mixture, washed with H_2O, dried, and redissolved in fresh CD_3CN. The ^{1}H NMR spectrum of the complex in the CD_3CN solution was identical with the spectrum shown in Figure 4a. From these results it is clear that no detectible H/D exchange occurs either during the NMR experiment or on a preparative time scale, thus ruling out protonation at bpy.

In a similar series of experiments the ^{1}H NMR spectrum of *trans*-[Os(bpy)(PPh_3)$_2$(CO)H]$^+$ was recorded in a 90% TFAD–10% TFMSH mixture. In this case the spectrum in the aromatic region was identical with the spectrum recorded in the protio acid, but the upfield resonance was absent. Isolation and dissolution of the complex in CD_3CN for ^{1}H NMR analysis after treatment with 90% TFAD–10% TFMSH, in the same manner described above for the bpy-d_8 analogue, showed that the aromatic region had not changed but the intensity of the Os–H triplet had decreased to ca. one-eighth of its original intensity.

The ^{1}H NMR results are consistent only with protonation at Os(II) to yield a formally seven-coordinate Os(IV) dihydride complex (eq 6). Rapid exchange of both Os–H protons with

$$(bpy)(PPh_3)_2(CO)Os{-}H^+ + H^+ \rightleftharpoons \left[(bpy)(PPh_3)_2(CO)Os\begin{matrix}H\\H\end{matrix}\right]^{2+} \quad (6)$$

deuterons explains the NMR spectral observation in the Os–H region. As previously discussed, the electronic spectral changes

(8) A reviewer offered the suggestion that eq 6 is slow in the presence of TFMSH because of a greatly decreased concentration of kinetically effective (basic) $CF_3CO_2^-$ ions upon addition of TFMSH. Experimental evidence supporting this hypothesis is provided by: Hanckel, J. M.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1983**, *105*, 6979. Stevens, R. E.; Gladfelter, W. L. *Ibid.* **1982**, *104*, 6454.

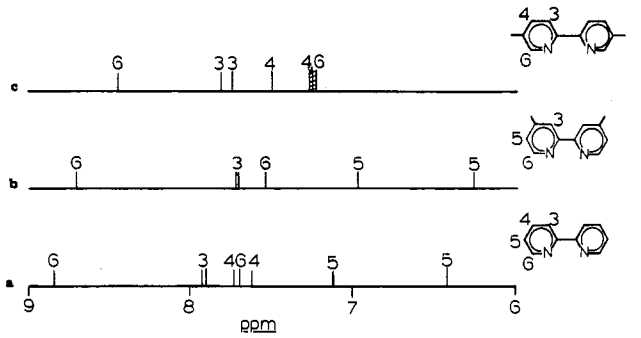


Figure 5. Shift correlation diagram for ^1H NMR spectral shifts in the series *trans*-$[Os(chelate)(PPh_3)_2(CO)H_2]^{2+}$: (a) chelate = bpy; (b) chelate = 4,4′-Me_2bpy; (c) chelate = 5,5′-Me_2bpy. The sticks in each diagram refer to the center of the multiplet, and the assignments are indicated above each stick.

in acidic media are also consistent with protonation at the metal.

Magnetic Symmetry of the Dihydrido–Os(IV) Complex. The broadened resonance in the Os–H region observed in acidic solution (Figures 3 and 4b) typically integrates to 1.5 protons. Metal hydride resonances in related d^6 six-coordinate Ir(III), Re(I), Os(II), and Ru(II)[2c,d] complexes have relaxation times that are similar to the proton resonances for the polypyridyl ligands. The less than expected integrated intensity may have its origin in a chemical exchange process involving the hydrido ligand. The appearance of the broadened resonance on addition of TFMSH suggests that the protonation equilibrium lies far to the right, but the large bandwidth (at half-height) for the resonance (ca. 10 Hz) suggests that exchange between the complex and the proton pool is still very rapid. Because of the exchange process any magnetic asymmetry at the two protons cannot be deduced from the room-temperature ^1H NMR spectral data. Unfortunately, attempts to "freeze-out" the proton exchange process by lowering the temperature of the acidic mixture to −5 °C were unsuccessful.

The $^{31}P\{^1H\}$ NMR spectrum of *trans*-$[Os(bpy)(PPh_3)_2(CO)H]^+$ in CH_3CN solution shows a single resonance at +19.3 ppm (from 85% H_3PO_4), consistent with equivalent PPh_3 ligands, as was previously deduced from the ^1H NMR spectrum in the phenyl region. The seven-coordinate complex $[Os(bpy)(PPh_3)_2(CO)H_2]^{2+}$ also exhibits a single $^{31}P\{^1H\}$ NMR resonance, which is shifted downfield (+7.7 ppm), indicating that a plane of symmetry which makes the PPh_3 groups equivalent in the starting complex is preserved in the protonated form.

Attempts to observe proton–phosphorus coupling in the dihydrido complex were not successful under a variety of conditions. For example, under conditions of irradiation at the frequency of the aromatic protons, the ^{31}P NMR spectrum of the parent complex shows a sharp doublet due to hydride–phosphorus spin–spin coupling (J_{PH} = 11 Hz at 25 °C in CH_3CN). The same experimental conditions for the complex in 90% TFAH–10% TFMSH at either 25 or −5 °C gave a slightly broadened singlet indicative of an exchange-decoupled system.

Complete Assignment of the ^1H NMR Spectrum for $[Os(bpy)(PPh_3)_2(CO)H_2]^{2+}$. The ^1H NMR spectra for the $[Os(chelate)(PPh_3)_2(CO)H_2]^+$ complexes (chelate = 5,5′-Me_2bpy, 4,4′-Me_2bpy, and bpy) under conditions of complete protonation, i.e., in 10% TFMSH–90% TFAH, were examined for first-order splittings and changes that occurred upon substitution of CH_3 for H. These are presented in the form of the stick diagram shown in Figure 5, which correlates the changes in proton shift between the derivatives. For the 5,5′-Me_2bpy case, one of the bpy resonances was coincident with a resonance arising from the PPh_3 groups; however, this does not affect the structural arguments presented below.

Seven-Coordinate Structure. Previous studies[9,10] have indicated

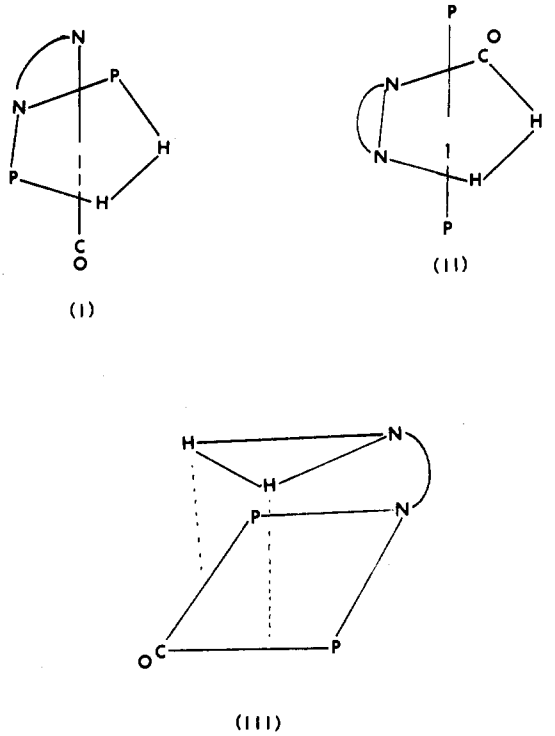


Figure 6. The three possible solution structures for $[Os(bpy)(PPh_3)_2(CO)H_2]^{2+}$. I and II are pentagonal bipyramidal, while III is based on the 4:3 geometry (see text).

that the bpy proton chemical shifts in metal polypyridyl complexes are primarily controlled by (a) the inductive effect of the N–metal bond, (b) the steric "bumping" of the protons in the 3,3′-positions, and (c) the proximity of the protons to either shielding or deshielding regions caused by the electronic distribution of the adjacent ligands, including ring-current effects from phenyl groups or pyridine ligands.

From the data shown in the NMR correlation diagrams (Figures 2 and 5) it can be seen that the relative ordering of chemical shifts is the same for $[Os(bpy)(PPh_3)_2(CO)H_2]^{2+}$ and its parent. This observation argues strongly for retention of an approximate "trans" relationship between the phosphine ligands and consequently a small amount of coordination sphere reorganization in the protonated form. The former point is convincingly demonstrated by consideration of a hypothetical complex where a bpy ligand and one PPh_3 group are in a mutually *mer* configuration. In this geometry, the 6,6′-protons, and possibly the 5,5′-protons as well, would lie in the shielding cone of the phenyl groups. The situation is similar to that found in complexes like *cis*-$(bpy)_2ML_2^{2+}$, where the 6′-proton of one bpy ligand is ca. 1–2 ppm upfield from the 6-proton of the remaining bpy ligand because of ring-current-induced diamagnetic anisotropy.[9b,c,10] The expectation in this case is that the relative ordering of the bpy proton chemical shifts would be more like that of complexes containing the *cis*-$M(bpy)_2^{n+}$ moiety and significantly different from that of the parent monohydride.

In order to assign the solution structure for $[Os(bpy)(PPh_3)_2(CO)H_2]^{2+}$, it is necessary to consider possible C_s seven-coordinate structures that possess a mirror plane containing the bpy ligand and having equivalent PPh_3 groups. Furthermore, structures containing cis-PPh_3 ligands are not considered reasonable since several synthetic studies have shown that only *trans*-$(PPh_3)_2$ polypyridine complexes can be isolated as stable compounds.[2c,6]

Of the eight possible C_s structures drawn from the idealized geometries pentagonal bipyramid (PBP), capped octahedron, capped trigonal prism, and the tetragonal-base–trigonal-base (4:3)

(9) (a) Constable, E. C.; Lewis, J. *Inorg. Chim. Acta* **1983**, *70*, 251. (b) Lytle, F. E.; Petrosky, L. M.; Carlson, L. R. *Anal. Chim. Acta* **1971**, *57*, 239. (c) Castellano, S.; Gunther, H.; Ebersole, S. *J. Phys. Chem.* **1965**, *69*, 4166.

(10) (a) DeSimone, R. E.; Drago, R. S. *Inorg. Chem.* **1969**, *8*, 2517. (b) Kahl, J. L.; Hanck, K.; DeArmond, K. *J. Inorg. Nucl. Chem.* **1979**, *41*, 495.

geometry, only three reasonable structures meet the above requirements. The possibilities include (Figure 6) one 4:3 geometry and two PBP's.[11]

Of the structures shown in Figure 6, the least likely is III (4:3), which requires a large amount of structural reorganization relative to the PBP's (I and II). We prefer structure II because the PPh_3–Os bond need elongate only slightly and protonation would result in expansion of the square plane containing three sterically nondemanding ligands, i.e., the two hydrides and a CO. In isomer I, expansion of the square plane would force the phosphines toward the bpy π cloud, and therefore I is a less satisfactory structure.

Concluding Remarks

Seven-coordination is unusual in the chemistry of Os(IV), as are high-oxidation-state Os polyhydrides. In this work we have described examples where both features are present in the same molecule. In a reactivity sense an important inference that can be drawn from our results is that seven-coordinate intermediates may play an important role in the formation of trifluoromethanesulfonate derivatives of octahedral precursors such as those shown in eq 1 and 2.

A striking contrast in behavior exists between the complexes discussed here and $[Os(bpy)_2(CO)H]^+$, where the reactivity with H^+ involves irreversible loss of H_2, presumably via initial protonation at Os.[12] Considered in that light, the reactions described here provide a conceptual link between electrophilic attack on low-spin d^6 metal centers and oxidative-addition reactions, both of which are uncommon for coordinatively saturated, octahedral precursors.

There is a final point to consider. The dihydrido complexes are thermally stable under ambient conditions so that the equilibrium in eq 7 *must* exist and might be observable if S is, for

$$[Os(bpy)(L)_2(CO)S]^{2+} + H_2 \rightleftharpoons [Os(bpy)(L)_2(CO)H_2]^{2+} + S \quad (7)$$

example, a weakly bound solvent molecule. The importance of reaction 7 is that it could provide a mechanistic basis for the activation of H_2 by d^6 octahedral metal complexes.[13]

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Registry No. *mer*-$Os(PPh_3)_3(CO)HCl$, 36007-23-5; *trans*-$[Os(PPh_3)_2(bpy)(CO)H](PF_6)$, 84117-37-3; *trans*-$[Os(PPh_3)_2(4,4'\text{-}Me_2bpy)(CO)H](PF_6)$, 106252-49-7; *trans*-$[Os(PPh_3)_2(5,5'\text{-}Me_2bpy)(CO)H](PF_6)$, 106252-51-1; *trans*-$[Os(PPh_3)_2(bpy\text{-}d_8)(CO)H](PF_6)$, 106252-53-3; *trans*-$[Os(PPh_3)_2(bpy)(CO)H_2]^{2+}$, 106267-39-4; *trans*-$[Os(PPh_3)_2(4,4'\text{-}Me_2bpy)(CO)H_2]^{2+}$, 106252-54-4; *trans*-$[Os(PPh_3)_2(5,5'\text{-}Me_2bpy)(CO)H_2]^{2+}$, 106252-55-5; *trans*-$[Os(PPh_3)_2(bpy\text{-}d_8)(CO)H_2]^{2+}$, 106252-56-6.

(11) We wish to thank a reviewer for a useful discussion of alternate structures.

(12) The electronic and steric features of metal hydrides that influence the base strength of the central metal, or even the hydridic vs. protonic character of the bond, have recently been discussed. See: Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.

(13) Brothers, P. J. *Prog. Inorg. Chem.* **1981**, *28*, 1-57 and references therein.

Contribution from the Department of Chemistry, Moscow State University, 119899 GSP, Moscow, USSR

Thermodynamics, Kinetics, and Mechanism of Exchange of Cyclopalladated Ligands

Alexander D. Ryabov

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The exchange between cyclopalladated complexes and free ligands has been studied in acetic acid. An equilibrium study of the system based on *N,N*-dimethylbenzylamine derivatives $[PdX(YZC_6H_2CH_2NMe_2)]_2 + 2C_6D_5CD_2NMe_2 \rightleftharpoons [PdX(C_6D_4CD_2NMe_2)]_2 + 2YZC_6H_2DCH_2NMe_2$ (K_1) has revealed that Pd(II) binds preferably with the electron-poorest ligand at equilibrium; K_1 is 114, 0.59, 0.125, 0.008, and 0.0034 for 4-Y (5-Z) = MeO (MeO), H (Me), H (H), H (Cl), and H (NO_2), respectively, at 55 °C in $D_3CCOOD/CDCl_3$, X = $MeCO_2^-$. A procedure for regioselective ortho palladation of "bifunctional" derivatives such as 1-(3,4-dimethoxyphenyl)-2-methyl-3-(4-nitrophenyl)-2-azapropane (**7**) is put forward. In aprotic chloroform, Pd(II) acetate metalates the electron-rich ring of **7** to yield **8a**, but the electron-poor ring is ortho palladated in acetic acid to yield **9a**. A dissociative exchange mechanism is proposed on the basis of a kinetic study of reactions between $[PdX(YZC_6H_2CH_2NMe_2)]_2$ and 2-phenylpyridine or azobenzene to afford the corresponding cyclopalladated complexes. Preequilibrium measurements have indicated that in the former case the reactive species are monomers formed via acetate-bridge cleavage by 2-phenylpyridine but in the latter case the complexes react as dimers. Despite this, all of the reactions are first order in complex and zero order in entering ligand. The rate constants of the 2-phenylpyridine case at 75 °C are (10^4k) 12.6, 3.9, 2.35, 2.6, 0.44, and 0.0225 s^{-1} for 4-Y (5-Z) = MeO (MeO), H (Me), H (H), H (MeO), H (Cl), and H (NO_2), respectively. On the basis of substituent and solvent kinetics isotope effects, values of activation parameters, and data obtained previously, it has been suggested that cleavage of the Pd–N bond of the leaving ligand occurs first, followed by acidolysis of the Pd–C bond. Both steps can contribute to the overall rate. The two are followed by the rapid activation of the C–H bond of the incoming ligand. Reasons for the pseudonucleophilic behavior of Pd(II) toward C–H bonds of benzylamines in acetic acid have been evaluated on the basis of the proposed mechanism.

Introduction

In the course of our study of vinylation of the ortho-palladated *N,N*-dimethylbenzylamine complex $[PdCl(C_6H_4CH_2NMe_2)]_2$ by styrenes, we found ortho-palladated *o*-((dimethylamino)methyl)stilbene derivatives.[1] The latter were formed due to a ligand exchange between the starting palladocycle and *o*-((dimethylamino)methyl)stilbene in the presence of acetic acid as cosolvent. Further efforts[2-7] have shown that ligand exchange may serve as an elegant synthetic procedure for the preparation of novel palladocycles (see Scheme I). In all cases the reactions are triggered by an addition of acetic acid to a solution of complex

(1) Ryabov, A. D.; Polyakov, V. A.; Yatsimirsky, A. K. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1503.
(2) Ryabov, A. D.; Yatsimirsky, A. K. *Inorg. Chem.* **1984**, *23*, 789.
(3) Ryabov, A. D.; Kazankov, G. M. *J. Organomet. Chem.* **1984**, *268*, 85.
(4) Ryabov, A. D. *Koord. Khim.* **1985**, *11*, 1532.
(5) (a) Ryabov, A. D.; Kazankov, G. M. *Koord. Khim.* **1986**, *12*, 540. (b) Ceder, R. M.; Granell, J.; Sales, J. *J. Organomet. Chem.* **1986**, *307*, C44. (c) Granell, J.; Sainz, D.; Sales, J.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1785.
(6) Ryabov, A. D.; Usatov, A. V.; Kalinin, V. N.; Zakharkin, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 2790.
(7) Ryabov, A. D.; Usatov, A. V.; Kalinin, V. N.; Zakharkin, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 1212.

0020-1669/87/1326-1252$01.50/0