A reexamination of the early stages of the thermal rearrangement of the naphthalene system **1** (k_8/k_1 = 4.0 at 193 °C) led to the observation, isolation, and demonstration of the intermediacy of analogous bicyclo[3.1.0]hexene precursors to **2** (namely, **6** and **7**), while verifying that **5** was not observable at any stage of the reaction.[17]

The probable mechanism for formation of the bicyclohexene products from **1** and **8** is given below. Thermal electrocyclic ring
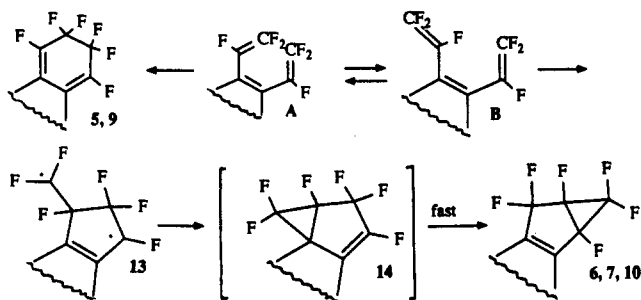
closure to orthoquinoid products **5** and **9** would have to occur from a conformation of the type A, which would maximize the steric and/or electrostatic repulsions of the fluorine substituents of the trifluorovinyl groups of **1** and **8**. It is likely because of such destabilizing interactions that a conformation of the type B ends up being the reactive one in these reactions.[18] Five-membered-ring formation from B will lead to diradical **13**, which, in a manner similar to that proposed for the photochemical process, can cyclize to a bicyclo[3.1.0]hexene species **14**, which will have lost considerable aromatic stabilization and thus should convert rapidly to the observed bicyclo[3.1.0]hexene products via a vinylcyclopropane rearrangement.

The actual observed thermolysis products can derive readily from such bicyclohexene intermediates via the diradical pathways shown below.[19] Note that a product analogous to **12** is not observed from **6** or **7**, while one like **4** is not formed from **10**.
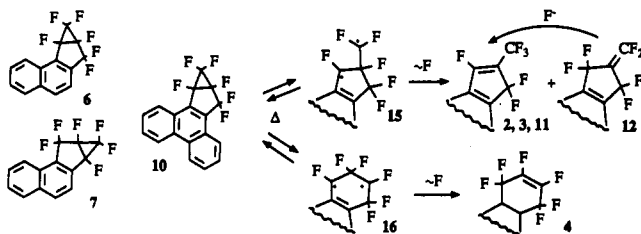
Examples of unambiguous *radical* rearrangements involving shift of F are themselves rare enough in the literature to be worthy of comment. While there is little doubt that F⁻-catalyzed rearrangements converting **12** to **11**,[21] as well as interconverting **2** and **3**, are intervening after long reaction times, it has been shown that the reactions leading to **6**, **7**, and **10** as well as to **2**, **3**, **4**, **11**, and **12** are *not* catalyzed by F⁻, and thus the intervention of diradical intermediates would appear to be unambiguously indicated in these reactions.

In conclusion, it has been observed that bis(trifluorovinyl) aromatics **1** and **8** undergo a novel thermal rearrangement in preference to the normal electrocyclic cyclization process. Further studies which will examine whether this new reaction extends to

fluorine-substituted acyclic 1,3,5-hexatriene systems are underway, and details regarding the interesting photochemistry of these systems will be reported soon.

Supplementary Material Available: Abbreviated experimental description of crystal data, data collection and reduction, and structure determination and refinement, table of experimental details, labeled ORTEP diagram, and tables of positional and thermal parameters, interatomic distances with esd's, interatomic angles with esd's, selected torsion angles, and least-squares planes with distances of selected atoms from planes for compound **3** (10 pages). Ordering information is given on any current masthead page.


Surface Intervalence Enhanced Raman Scattering from Fe(CN)₆⁴⁻ on Colloidal Titanium Dioxide. A Mode-by-Mode Description of the Franck–Condon Barrier to Interfacial Charge Transfer

Robert L. Blackbourn, Christopher S. Johnson, and Joseph T. Hupp*

Department of Chemistry, Northwestern University
Evanston, Illinois 60208-3113

Received September 12, 1990

One of the key requirements in any quantitative description of electron-transfer kinetics, in any environment, is an accurate estimate of internal or vibrational reorganization energetics.[1] We have recently shown that complete mode-by-mode descriptions of vibrational reorganization for selected metal-to-ligand[2] and metal-to-metal (or intervalence)[3] charge-transfer events in solution can be obtained by applying time-dependent scattering theory[4,5] to pre- or postresonance Raman spectra.[6] The quantities obtained are redox-induced normal coordinate displacements (Δ), force constants (f), and individual components (χ_i') of the total vibrational reorganization energy (χ_i). We now report an extension of this methodology to an *interfacial* charge transfer reaction.

The reaction chosen was optical electron transfer from Fe-$(CN)_6^{4-}$ to colloidal titanium dioxide:[7,8]

(1)

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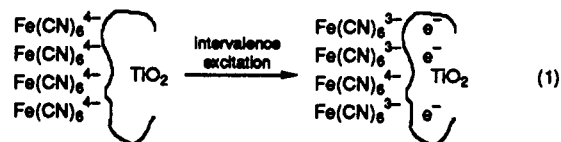
(1) For general reviews, see: (a) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (b) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (c) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437.

(2) Doorn, S. K.; Hupp, J. T. *J. Am. Chem. Soc.* **1989**, *111*, 4704.

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(4) (a) Heller, E. J.; Sundberg, R. L.; Tannor, D. *J. Phys. Chem.* **1982**, *86*, 1822. (b) Tannor, D. J.; Heller, E. J. *J. Chem. Phys.* **1982**, *77*, 202. (c) Lee, S. Y.; Heller, E. J. *J. Chem. Phys.* **1977**, *71*, 4777. (d) Heller, E. J. *Acc. Chem. Res.* **1981**, *14*, 368. (e) Morris, D. E.; Woodruff, W. H. *J. Phys. Chem.* **1985**, *89*, 5795.

(5) See also: (a) Warshel, A.; Dauber, P. *J. Chem. Phys.* **1977**, *66*, 5477. (b) Myers, A. B.; Mathies, R. A. In *Biological Applications of Raman Spectroscopy*; Spiro, T. G., Ed.; John Wiley and Sons: New York, 1987; Vol. 2. (c) Schomacher, K. T.; Bangcharoenpaurpong, O.; Champion, P. M. *J. Chem. Phys.* **1984**, *80*, 4701. (d) Hizhnyakov, V.; Tehver, I. *J. Raman Spectrosc.* **1988**, *19*, 383.

(6) Related experimental applications of time-dependent Raman scattering theory: (a) Tutt, L.; Zink, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 5830. (b) Zink, J. I.; Tutt, L.; Yang, Y. Y. *ACS Symp. Ser.* **1986**, *307*, 39. (c) Yang, Y. Y.; Zink, J. I. *J. Am. Chem. Soc.* **1985**, *107*, 4799. (d) Tutt, L.; Tannor, D.; Heller, E. J.; Zink, J. I. *Inorg. Chem.* **1982**, *21*, 3858. (e) Zink, J. I. *Coord. Chem. Rev.* **1985**, *64*, 93. (f) Truhlson, M. O.; Dollinger, G. D.; Mathies, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 586.

(7) Vrachnou, E.; Grätzel, M.; McEvoy, A. J. *J. Electroanal. Chem.* **1989**, *258*, 193.

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(17) Photolysis of **1** resulted in the formation of **5** as the major product.[13] **5** could also be characterized via its Diels-Alder reaction with diethyl acetylenedicarboxylate.

(18) The relative thermodynamics of the two systems **1** and **8** probably dictates why **5** is not formed thermally from **1** while formation of **9** from **8** at least competes with the new cyclization process.

(19) There is precedent for the observed rearrangement of the perfluorinated bicyclo[3.1.0]hexene system in the reported high-temperature reaction of CF₂ with perfluoroindene.[20]

(20) Karpov, V. M.; Platonov, V. E.; Stolyarova, T. A.; Yakobson, G. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 1586.

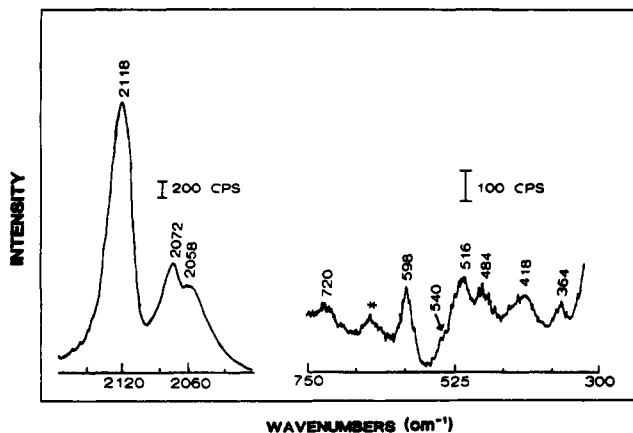(21) Conversion of **12** to **11** is very rapid upon addition of traces of F⁻ to the product mixture.

Communications to the Editor

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Figure 1. Preresonance Raman spectrum of 0.6 mM $Fe(CN)_6^{4-}$/(5.8 g/L TiO_2) colloid at pH = 2.0 with 488.0-nm excitation. The asterisk at 656 cm^{-1} denotes an unenhanced E_g mode of TiO_2. The mode at 540 cm^{-1} is real and is more convincingly resolved in experiments performed at 457.9 nm.

Following Vrachnou and co-workers,[7] we find that an intense optical absorption exists ($\lambda_{max} \approx 410$ nm, $\epsilon \approx 5000$ M^{-1} cm^{-1}) for the "surface intervalence" charge-transfer reaction in eq 1. We further find (Figure 1) that Raman scattering spectra can be readily obtained based on near-resonant excitation (488 nm).[9] Control experiments at 514.5 nm (nominally preresonant), at 647.1 nm (off resonance), with ferrocyanide alone and with colloidal TiO_2 alone, all show the scattering in Figure 1 to be resonantly enhanced (e.g., enhancement factors of at least 20 for the highest energy modes).[10,11]

The observation of enhancement is of central importance: within the context of the time-dependent theory,[4,5] resonance enhancement (Albrecht A-term scattering) indicates the displacement of normal coordinates in direct response to the pertinent electronic transition (in our case, eq 1). In the simplest case, the quantitative relationships between scattering intensity (I) and molecular structural changes are[4]

$$I_1/I_2 = \omega_1^2 \Delta_1^2 / \omega_2^2 \Delta_2^2 \qquad (2)$$

$$\chi_i = 0.5 \sum_k \Delta_k^2 (\omega_k/2\pi) \qquad (3)$$

where ω is 2π times the vibrational frequency and the summation

Table I. Spectroscopic, Structural, and Reorganizational Parameters for Electron Transfer from $Fe(CN)_6^{4-}$ to Colloidal TiO_2

mode (cm^{-1})	rel int[a,b]	Δ^2	$|\Delta a|$ (Å)	χ_i (cm^{-1})	assignment
2118	20.0	0.95[c]	0.048	1000	ν_{C-N} bridge
2072	6.61	0.33	0.014	340	ν_{C-N} radical
2058	5.44	0.27	0.026	280	ν_{C-N} terminal
720	0.27	0.11	?	40	?
598	1.00	0.59	0.026[d]	180	ν_{Fe-C}
540	0.33	0.24	0.039	60	ν_{Fe-C} bridge
516	1.12	0.89	e	230	ν_{Ti-O}
484	0.90	0.82	e	200	ν_{Ti-O}
418	0.56	0.69	e	140	ν_{Ti-O}
364	0.27	0.43	0.059	80	ν_{Ti-N}

[a] Depolarization studies indicate that all modes, with the possible exception of modes at 540 and 720 cm^{-1} (too weak to determine with certainty), are totally symmetric. [b] Within the experimental uncertainty, *relative* intensities are unaffected by changes in excitation wavelength. [c] All values scaled to the value for Δ^2 at 598 cm^{-1}. [d] Taken from (or taken as) the crystallographically determined value[12] for $Fe(CN)_6^{4-/3-}$. [e] Value not determined, since the measured normal coordinate displacement (Δ) may entail more than one type of bond-length displacement (i.e., a local-mode approximation may not be appropriate).

is over all modes which are significantly resonantly enhanced. If a local mode approximation is appropriate, absolute bond length changes ($|\Delta a|$) can also be obtained:[2,4]

$$(|\Delta a|) = (\Delta^2 \hbar / \mu \omega b)^{1/2} \qquad (4)$$

In eq 4, μ is the reduced mass and b is the bond degeneracy.

Table I lists the relative intensities, unitless normal coordinate displacements, and bond-length changes obtained for resonance-enhanced modes. Absolute Δ and Δa values were derived by assuming that the changes in length for nonbridging Fe–C bonds equaled those determined crystallographically for free $Fe(CN)_6^{3-/4-}$.[12] Mode assignments were made by analogy to $Fe(CN)_6^{4-}$,[13] $(H_3N)_5RuNCFe(CN)_5^{1-}$, $(H_3N)_5OsNCFe(CN)_5^{1-}$, and related systems[3] and will be described in greater detail elsewhere. From the table, a number of points are worth noting: (1) The total number of modes (or types of bonds) displaced is surprisingly large (10), indicating that even the simplest of interfacial redox reactions may entail substantial complexity in vibrational activation. (2) As seen for related binuclear metal systems (in solution),[3] bridging modes suffer the greatest displacement, with the C≡N bridging mode providing the largest single contribution to the vibrational barrier. (3) Remarkably, three *surface* modes are enhanced and therefore displaced during optical electron transfer. This last observation is unprecedented experimentally and is at odds with most, if not all, existing theoretical views of interfacial electron transfer.

While the mode assignments in Table I are reasonably well established, questions do arise regarding the possibility of more than one type of binding geometry (e.g., doubly bridged) and the degree of protonation of the bound ferrocyanide. We performed a number of control experiments where (1) $Fe(CN)_6^{4-}$ and colloidal TiO_2 concentrations were substantially varied, (2) the pH was varied between 1 and 3, (3) multiple excitation wavelengths were used in resonance, and (4) an isotope study using a 7:1 dilution in D_2SO_4/D_2O was completed. Interestingly, all of these experiments led to no change in relative Raman intensities or frequency shifts. These results, therefore, tend to support the notion that only one type of complexed ferrocyanide species exists, which apparently is unprotonated and is bound to titanium via a single-cyanide ligand.[14]

Finally, the possibility of unwanted scattering from either a Prussian blue or titanate/$Fe(CN)_6^{4-}$ species was considered. We

(8) Colloidal TiO_2 sols were prepared by following the method used in ref 7. We found that agitation and slow addition of potassium ferrocyanide solutions to the dialyzed and diluted colloid produced stable charge-transfer assemblies. For Raman studies (excitation at 457.9, 488.0, 514.5, and 647.1 nm), the colloidal sols contained approximately 10^{-4} mol of $Fe(CN)_6^{4-}$/g of TiO_2; higher loadings led to sol aggregation and then precipitation. Ferrocyanide concentrations ranged from 0.1 to 1.0 mM. In a few experiments, NO_3^- or methanol was added as an internal intensity standard. The sol pH was varied between 1 and 3 (chiefly by varying dialysis times and the number of dialysis steps) with no variations found in the enhanced scattering spectra. It should be noted that at the low pH's used in this study, polyvinyl alcohol (a common colloid stabilizer) was not needed.

(9) Raman spectra were obtained with a windowless flow cell under an argon blanket. Chromophore concentrations were chosen so as to minimize complications from self-absorption. Typically, a bandpass of 9 cm^{-1} was employed with 40–60 mW of incident excitation power. For weak portions of the spectrum, signals were sometimes averaged (with appropriate checks for system drift) for as long as 20 h. We note further that background counts in the low-energy end of the spectrum (ca. 750–300 cm^{-1}; see Figure 1) were often as high as 5000/s, rendering signal extraction somewhat difficult. Our results stand in marked contrast to those of Umapathy, McQuillan, and Hester (*Chem. Phys. Lett.* **1990**, *170*, 128), who very recently reported observing only the two highest frequency modes seen in our spectrum. The precautions described above no doubt account for the exceptional differences between our findings and those reported elsewhere.

(10) In addition, very weak, unenhanced modes at 656 and 920 cm^{-1} were occasionally found, as was a stronger mode (also unenhanced) at 1641 cm^{-1}. Lack of enhancement indicates lack of participation of these modes in vibrational reorganization.

(11) Intensities have been corrected for residual self-absorption (Shriver, D. F.; Dunn, J. B. R. *Appl. Spectrosc.* **1974**, *28*, 319) and for ν^4 attenuation effects.

(12) Swanson, B. I.; Hamburg, S. I.; Ryan, R. R. *Inorg. Chem.* **1974**, *13*, 1685.

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(14) If, in fact, two cyanide ligands serve as bridges, Δa (ν_{C-N} bridge) decreases to 0.032 Å; most other Δa values would be diminished by about 10%.

eliminated the Prussian blue problem by (1) using $Os(CN)_6^{4-}$ in place of $Fe(CN)_6^{4-}$ with similar results, (2) purposely making the Prussian blue complex which absorbs in the red and showing that it is not present in our absorption spectrum, and (3) proving that no enhancement occurs in the $Fe(CN)_6^{4-}$/colloidal-TiO_2 solution at 647.1 nm (where Prussian blue would absorb). The second problem, titanate formation during preparative $TiCl_4$ hydrolysis, can be effectively eliminated by dialysis.[7] This was confirmed by an electrochemical experiment (supplementary material) in which redox-active $Fe(CN)_6^{4-}$ (i.e., free or titanate bound) was shown to be absent from $Fe(CN)_6^{4-}$/dialyzed-colloid solutions, but present in intentionally prepared $Fe(CN)_6^{4-}$/titanate solutions.[15]

Supplementary Material Available: One figure showing differential pulse voltammograms for $Fe(CN)_6^{4-}$/colloidal-TiO_2 and $Fe(CN)_6^{4-}$/titanate solutions (1 page). Ordering information is given on any current masthead page.

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(15) The source of titanate was the outer portion of a colloidal-TiO_2 dialysis solution. See ref 7 for related experiments.

Complexation through Nitrogen in Copper and Nickel Complexes of Substituted Ureas[†]

Przemyslaw Maslak,*,[1a] John J. Sczepanski,[1a] and Masood Parvez[1b]

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802
Department of Chemistry, The University of Calgary
Calgary, Alberta, Canada T2N 1N4

Received October 3, 1990

Complexation of transition metals by biologically relevant ligands, such as the prevalent amide ($>$N$-$C$=$O) functionality, has attracted considerable attention due to the catalytic potential of such complexes.[2-4] In principle, transition-metal ions can

Figure 1. ORTEP drawing of the Cu(II) complex of **1a**. Selected bond lengths (Å) and angles (deg) are as follows: Cu–N1, 1.998 (9); Cu–N2, 2.127 (9); Cu–Cl1, 2.241 (3); Cu–Cl2, 2.229 (3); C7–O, 1.22 (1); C7–N2, 1.45 (2); C7–N3, 1.32 (2); C6–N2, 1.48 (2); Cl1–Cu–Cl2, 93.2 (1); Cl1–Cu–N1, 96.8 (3); Cl1–Cu–N2, 166.5 (4); Cl2–Cu–N1, 169.9 (3); Cl2–Cu–N2, 88.9 (3); N1–Cu–N2, 81.8 (3); Cu–N2–C6, 105.2 (6); Cu–N2–C7, 113.2 (7); O–C7–N2, 119 (2); O–C7–N3, 125 (1).
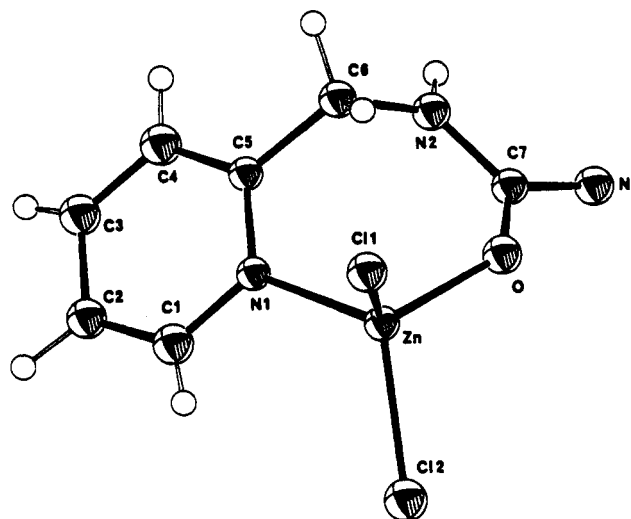
Figure 2. ORTEP drawing of the Zn(II) complex of **1a**. Selected bond lengths (Å) and angles (deg) are as follows: Zn–N1, 2.035 (4); Zn–O, 1.981 (4); Zn–Cl1, 2.234 (2); Zn–Cl2, 2.231 (2); C7–O, 1.263 (7); C7–N2, 1.359 (6); C7–N3, 1.317 (8); C6–N2, 1.449 (9); Cl1–Zn–Cl2, 110.36 (8); Cl1–Zn–N1, 112.3 (1); Cl1–Zn–O, 114.9 (1); Cl2–Zn–N1, 111.6 (1); Cl2–Zn–O, 107.7 (1); O–Zn–N1, 99.4 (2); Zn–O–C7, 135.9 (3); Zn–N1–C5, 122.7 (3); O–C7–N2, 121.9 (6); O–C7–N3, 121.2 (4).

complex to ureas and amides via oxygen or nitrogen atoms. The oxygen lone pair is more basic than the nitrogen site. In the case of amides, the basicity difference toward protons is estimated as seven pK_a units.[5] A similar situation exists in ureas.[6] In accord with these basicity differences, complexes of ureas[7,8] or uncharged

†This paper is dedicated to Professor Ronald Breslow.
(1) (a) The Pennsylvania State University. (b) The University of Calgary.
(2) For a review, see: (a) Freeman, H. C. In *Inorganic Biochemistry*; Eichhorn, G. L., Ed.; Elsevier: New York, 1973; p 121. (b) Sigel, H., Ed. *Metal Ions in Biological Systems*; Marcel Dekker: New York, 1973; Vol 2. (c) Ochiai, E.-I. *General Principles of Biochemistry of the Elements*; Plenum Press: New York, 1987. (d) Murzubraimov, B. *Koord. Khim.* **1985**, *11*, 158.
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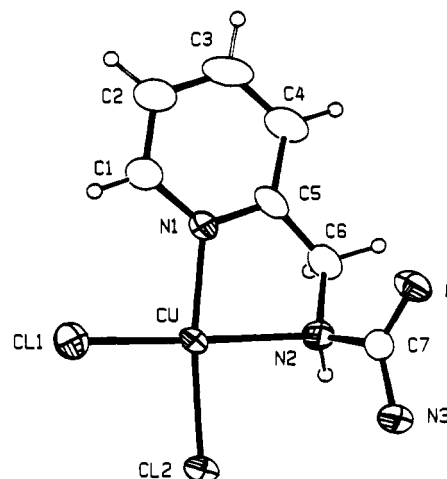
(5) (a) Perrin, C. L.; Lollo, C. P.; Johnston, E. R. *J. Am. Chem. Soc.* **1984**, *106*, 2749, 2754. (b) Fersht, A. R. *J. Am. Chem. Soc.* **1971**, *93*, 3504.
(6) Tetramethylurea is very similar to *N,N*-dimethylacetamide in its ability to form hydrogen bonds through the oxygen atom. Also, in both cases the protonation in fluorosulfuric acid takes place at oxygen atom: Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875.
(7) Urea complexes have been characterized only by IR spectroscopy as to the mode of coordination. With a few exceptions (ref 8) the data are consistent with O-coordination. There seems to be no X-ray structure of such complexes available. See, for example: (a) Murzubraimov, B.; Toktomamatov, A. *Koord. Khim.* **1983**, *9*, 601. (b) Srivastava, P. C.; Aravindakshan, C. *Z. Phys. Chem. (Leipzig)* **1983**, *264*, 61. (c) Bailey, R. A.; Feins, I. R.; Peterson, T. R. *Can. J. Chem.* **1969**, *47*, 171. (d) Muksumova, Z. S.; Orozbaeva, N. O.; Fridman, Y. D.; Molodkin, A. K.; Rysmendeev, K. *Zh. Neorg. Khim.* **1986**, *31*, 2865. (e) Sharma, S. B.; Singh, V. P.; Singh, M. K.; Sharma, S. K. *J. Indian Chem. Soc.* **1985**, *62*, 721.