somewhat from those in *cis*-[Pt(NH$_3$)$_2${d(pGpG)}]. Base/base dihedral angles in the theoretical models range from 50°–66°, a significant reduction from the angles observed here. Moreover, diminished N7–Pt–N7 angles of 79°–82° occur in the models from molecular mechanics calculations, which partly accounts for the smaller base/base dihedral angles. Comparatively reduced base/PtN$_4$ angles, ranging from 52°–85°, are also observed in the theoretical double-stranded models. Comparisons between B-DNA and *cis*-[Pt(NH$_3$)$_2${d(pGpG)}] in Figure 11 suggest that the structures revealed by the present X-ray study could not exist in double-stranded DNA without either significant disruption of hydrogen bonds involved in Watson–Crick base pairing or considerable distortion of the complementary strand. The gel electrophoresis data suggest DNA bending of ~40°±5° accompanies formation of the d(GpG) *cis*-diammineplatinum(II) crosslink. Such a distortion in the duplex would undoubtedly influence cellular phenomena such as DNA repair.

The crystallization and X-ray structural elucidation of platinum complexes of double-stranded oligonucleotides would provide much needed structural information about both the site of platination and duplex perturbations several base pairs away from the site of platination. Such information would be very helpful in interpreting the results of the biochemical processing of DNA, both in vitro and in vivo.[65] Crystallization of *cis*-diammineplatinum(II) adducts with single-stranded oligonucleotides containing extra bases at the 5′- or 3′-ends of d(pGpG) will probably not supply much additional information to that which we already have. As in the case of the 5′-cytosine in the X-ray structure of *cis*-[Pt(NH$_3$)$_2${d(CpGpG)}], the conformations of 5′- or 3′-bases in single-stranded oligonucleotides will be highly influenced by crystal packing forces in the solid state. X-ray studies of other adducts formed by *cis*-DDP and adducts formed by *trans*-DDP, however, will provide needed structural information.

Acknowledgment. This work was supported by U.S. Public Health Service Grant CA 34992 (to S.J.L.) from the National Cancer Institute. D.G. was a Chain Weizmann Postdoctoral Fellow. Helpful discussions, advice, and experimental assistance were provided by Professor G. Petsko, Drs. G. J. Quigley, J. Kozelka, P. Shing Ho, C. Frederick, P. Mascharak, and R. Campbell, to whom we are grateful. We also thank the Engelhard Corporation for a loan of K$_2$PtCl$_4$ from which the platinum dinucleotide complex was prepared.

Registry No. *cis*-[Pt(NH$_3$)$_2$(d(pGpG))], 81119-95-1.

Supplementary Material Available: Tables of atomic positional and thermal parameters (Tables S2 and S3), interatomic bond distances and angles (Tables S4 and S5), and best planes calculations (Table S6) (17 pages); observed and calculated structure factor amplitudes (Table S1) (61 pages). Ordering information is given on any current masthead page.

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Ruthenium(II) 2,2′-Bipyridine Complexes Containing Methyl Isocyanide Ligands. Extreme Effects of Nonchromophoric Ligands on Excited-State Properties

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Abstract: The new isocyanide complexes Ru(bpy)$_2$(CN)(CNMe)$^+$, Ru(bpy)$_2$(CNMe)$_2$$^{2+}$, and Ru(bpy)(CNMe)$_4$$^{2+}$ have been synthesized, and their photophysical and redox behavior has been studied in detail. With respect to the cyanide analogues, the strong electron-withdrawing effect of the methyl isocyanide ligands causes (i) large blue shifts in the Ru→bpy MLCT transitions and (ii) large anodic shifts in the potentials for oxidation of Ru(II). The excited-state behavior of Ru(bpy)(CNMe)$_4$$^{2+}$ appears quite exceptional with respect to that of common Ru(II) bipyridine complexes. In fact (i) its lowest excited state is a long lived (τ = 8.8 μs in water at 298 K) bpy-centered π–π* state and (ii) the complex is a strong excited-state oxidant ($E_{1/2}$(*Ru(III)/Ru(II)) = +1.49 V vs SCE in MeCN). This constitutes a rather extreme example of tuning of excited-state properties by nonchromophoric ligands.

Because of its outstanding excited-state properties, tris(2,2′-bipyridine)ruthenium(II), Ru(bpy)$_3$$^{2+}$, has been one of the most extensively studied and widely used molecules in research laboratories during the last 10 years.[1-3] It is now clear that, at least in room temperature fluid solution, the d–π* metal-to-ligand charge transfer (MLCT) excited state of Ru(bpy)$_3$$^{2+}$ is localized on a single Ru–bpy unit.[4] Common mono- or bis-2,2′-bipyridine (2,2′-bipyridine = bpy) ruthenium(II) complexes containing non-polypyridine ancillary ligands, however, do not exhibit the outstanding excited-state properties of the parent Ru(bpy)$_3$$^{2+}$ complex.[2,3] This is generally due to fast deactivation of the relevant Ru–bpy d–π* (MLCT) excited state occurring via low-lying d–d metal centered (MC) states.[5-7] The only way to avoid this process and to obtain mono- and bis-bpy Ru(II) complexes of appreciable excited-state lifetime is to use very strong field nonchromophoric ligands. Thus, mixed cyanide–bpy complexes such as Ru(bpy)$_2$(CN)$_2$[8] and, more recently, Ru(bpy)(CN)$_4$$^{2-}$[9] have been

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Table I. Spectroscopic Properties[a]

	$Ru(bpy)_2Y$, Y =			$Ru(bpy)Y$, Y =	
	$(CN)_2$	$(CN)(CNMe)^+$	$(CNMe)_2^{2+}$	$(CN)_4^{2-}$	$(CNMe)_4^{2+}$
$\bar{\nu}_{max}^{abs}(H_2O)$,[b] μm^{-1}	2.32	2.59	2.78	2.50	3.25
$\bar{\nu}_{max}^{abs}(MeCN)$,[b] μm^{-1}	2.02	2.44	2.78	1.90	3.25
$\bar{\nu}_{max}^{em}(H_2O)$, μm^{-1}	1.58	1.69		1.58	2.10
$\bar{\nu}_{max}^{em}(MeCN)$, μm^{-1}	1.46	1.66		1.26	2.10
$\tau_{298\ K}(H_2O)$,[c] ns	250	5		101	8.8×10^3
$\tau_{298\ K}(MeCN)$,[c] ns	240	21		7	6.0×10^3
$\tau_{77\ K}$,[d] μs	4	11	15	2	220

[a] Room temperature. [b] Maxima of the lowest energy band. [c] Deaerated solution. [d] Absolute ethanol glass.

shown to have long-lived, emitting MLCT excited states in fluid solution. Because of the tendency of the cyanide ligands to give second-sphere donor–acceptor interactions,[10] the spectroscopic, photophysical, and redox properties of $Ru(bpy)_2(CN)_2$ and $Ru(bpy)(CN)_4^{2-}$ are extremely sensitive to the environment.[8-15] This feature is intrinsically interesting and may prove useful for use of these molecules as probes of various types of environments. On the other hand, it may constitute a limitation for the practical use of these complexes as photosensitizers.

In principle, complexes containing bipyridine and *isocyanide* ligands could have interesting excited-state properties. In fact, isocyanide ligands are expected to provide a strong ligand field,[16] thus keeping the MC states at high energies and slowing down radiationless deactivation. Complexes of this type are not known, however, and relatively little information is available on isocyanide complexes of Ru(II) as a whole.[2] Thus, the chemistry and the excited-state properties of mixed-ligand bipyridine–isocyanide complexes of Ru(II) are not easily predictable. As a first step in this direction, we have now synthesized the following methyl isocyanide complexes: $Ru(bpy)_2(CN)(CNMe)^+$, $Ru(bpy)_2(CNMe)_2^{2+}$, and $Ru(bpy)(CNMe)_4^{2+}$. We describe here the photophysical behavior and the ground- and excited-state redox properties of these new species. For some of the methyl isocyanide complexes, notably for $Ru(bpy)(CNMe)_4^{2+}$, excited-state properties are observed that are rather exceptional with respect to those of most other Ru(II) polypyridine complexes.

Experimental Section

Materials. $[Ru(bpy)_3]Cl_2$ (Carlo Erba), dimethyl sulfate (Fluka), and the methoxybenzenes (Fluka) were commercial products of reagent grade. $[Ru(bpy)_3](ClO_4)_3$ was prepared following a literature procedure.[17] *cis*-$Ru(bpy)_2(CN)_2$[12] and $K_2[Ru(bpy)(CN)_4]$[9] were available from previous work. Spectrograde organic solvents (Merck Uvasol) and triply distilled water were used.

Syntheses. The complexes were prepared with procedures similar to that reported by Balch for $[Fe(phen)_2(CNMe)_2](PF_6)_2$.[18]

$[Ru(bpy)_2(CNMe)_2](PF_6)_2$. A suspension of anhydrous *cis*-$Ru(bpy)_2(CN)_2$ (0.5 g) in dimethyl sulfate (10 mL) was stirred for 2 h at 70 °C. The resulting yellow solution was extracted with three 10-mL portions of water. The product was precipitated from the aqueous solution by addition of a saturated aqueous solution of NH_4PF_6. The product was redissolved in water and purified by ion exchange chromatography with Sephadex SP-C25 cation-exchange resin. Some unreacted $Ru(bpy)_2(CN)_2$ was first eluted with water; then, elution was continued with 0.05 M NaCl to remove a small amount of $[Ru(bpy)_2(CN)(CNMe)]Cl$. The desired product was collected with 0.1 M NaCl as eluant, precipitated by addition of NH_4PF_6, and dried under vacuum. Yield, 90%. Anal. Calcd for $[Ru(bpy)_2(CNMe)_2](PF_6)_2$: C, 36.70; H, 2.82; N, 10.70. Found: C, 36.55; H, 2.70; N, 10.73.

$[Ru(bpy)(CN)(CNMe)]PF_6$. The same procedure used for $[Ru(bpy)_2(CNMe)_2](PF_6)_2$ was followed, except that the reaction time was decreased to 20 min. In this case, the chromatographic fraction containing the desired complex was that eluted with 0.05 M NaCl. Yield, 40%. Anal. Calcd for $[Ru(bpy)_2(CN)(CNMe)](PF_6)$: C, 44.16; H, 3.06; N, 13.44. Found: C, 43.42; H, 2.93; N, 13.27.

$[Ru(bpy)(CNMe)_4](PF_6)_2$. A suspension of anhydrous $K_2[Ru(bpy)(CN)_4]$ (0.5 g) in dimethyl sulfate (10 mL) was stirred at 95 °C for 6 h. The product was isolated as hexafluorophosphate salt as reported for $[Ru(bpy)_2(CNMe)_2](PF_6)_2$ and purified from trace polymeric impurities by chromatography on Sephadex SP-C25 resin. The colorless complex was eluted from the column with 0.1 M NaCl; the yellow polymeric impurities were retained in the column (and could be eventually eluted with 1 M NaCl). Yield, 90%. Anal. Calcd for $[Ru(bpy)(CNMe)_4](PF_6)_2$: C, 30.39; H, 2.83; N, 11.81. Found: C, 30.10, H, 2.80; N, 11.88.

Apparatus and Procedures. UV-vis spectra were recorded with a Varian Cary 219 spectrophotometer. The emission spectra were measured with a Perkin-Elmer MPF 44E spectrofluorimeter equipped with a R 928 Hamamatsu tube. All the emission spectra were corrected by calibrating the instrumental response with respect to a NBS standard quartz tungsten–halogen lamp. Emission quantum yield values were obtained by using $Ru(bpy)_3^{2+}$ ($\Phi = 0.042$)[1] as a reference emitter. The emission lifetimes were measured with a J & K System 2000 ruby laser (frequency doubled, pulse half-width 20 ns) in a single shot mode with oscillographic recording, or with a PRA system 3000 nanosecond fluorescence spectrometer equipped with a 510B nanosecond pulsed lamp and a Model 1551 cooled photomultiplier (data collected on a Tracor Northern TN1750 multichannel analyzer and processed with original PRA software). ESA spectra were measured by using a laser flash photolysis apparatus (Applied Photophysics detection system coupled with the J & K System 2000 ruby laser source). Infrared spectra were recorded with a Perkin-Elmer Model 283 spectrophotometer in KBr pellets. Proton NMR spectra were recorded on a Bruker WP-80 spectrometer operating at 80 MHz.

In electron-transfer quenching experiments, the bimolecular quenching constants, k_q, were obtained from emission lifetime Stern–Volmer plots. The quantum yields of formation of transient redox products, Φ_{ce}, and the rate constants of the back-electron transfer reaction, k_b, were measured on deaerated solutions by laser photolysis following previously described procedures.[12]

Low-temperature emission spectra and lifetimes were measured by using Oxford Instruments DN 704 cryostatic equipment with quartz windows and standard 1-cm spectrofluorimetric cuvettes.

Cyclic voltammetry was performed on Ar-purged MeCN and DMF solutions containing 0.1 M [TEA]TFB with an Amel 448 oscillographic polarograph. A conventional three-electrode cell was used in all the experiments. A saturated calomel electrode (SCE) was used as reference electrode; the auxiliary electrode was a platinum wire; a platinum microsphere and a hanging mercury electrode (HME) were used as working electrodes. Controlled-potential electrolyses were performed with an Amel 568 programmable function generator and with an Amel 552 potentiostat. Spectra of electrochemically reduced species were obtained with an OTTLE (optically transparent thin-layer electrode) made of a platinum 90% rhodium 10% grid (Johnson Mattey) placed between the windows of a 2-mm spectrophotometric cell directly mounted on a Perkin-Elmer 323 spectrophotometer. The counterelectrode was a Pt wire separated from the cathodic compartment by a frit; an Ag wire was used as reference electrode.

Results

General Properties. Hexafluorophosphate salts of $Ru(bpy)_2(CN)(CNMe)^+$, $Ru(bpy)_2(CNMe)_2^{2+}$, and $Ru(bpy)(CNMe)_4^{2+}$

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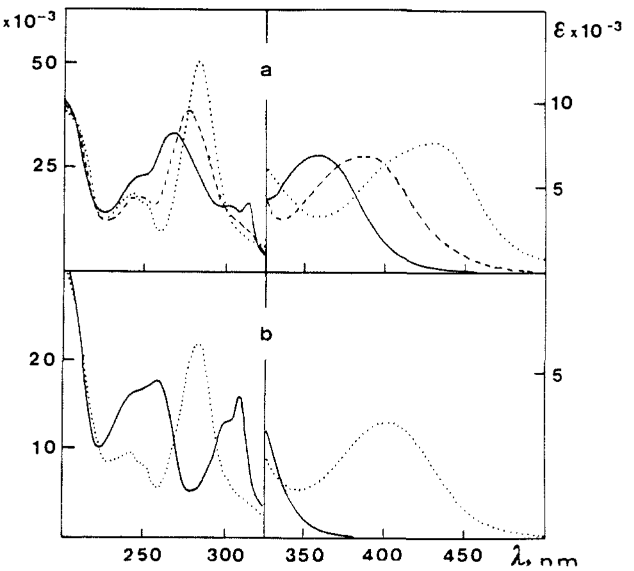

Figure 1. Absorption spectra in aqueous solution of (a) $Ru(bpy)_2(CN)_2$ (···), $Ru(bpy)_2(CN)(CNMe)^+$ (- - -), $Ru(bpy)_2(CNMe)_2^{2+}$ (—) and (b) $Ru(bpy)(CN)_4^{2-}$ (···), $Ru(bpy)(CNMe)_4^{2+}$ (—).

Table II. Ground- and Excited-State Redox Potentials[a]

	$Ru(bpy)_2Y$, Y =			$Ru(bpy)Y$, Y =	
	$(CN)_2$	(CN)- $(CNMe)^+$	$(CNMe)_2^{2+}$	$(CN)_4^{2-}$	$(CNMe)_4^{2+}$
$E_{1/2}^{\text{ox}}$,[b] V	+0.85	+1.35	+1.88	+0.27	+2.37
$E_{1/2}^{\text{red}}$,[b] V	−1.65	−1.47	−1.33	−1.95[c]	−1.33
E^{0-0},[d] eV	2.05[e]	2.34	2.63	2.03[e]	2.82
$^*E_{1/2}^{\text{ox}}$, V	−1.2	−0.99	−0.75	−1.76	−0.45
$^*E_{1/2}^{\text{red}}$, V	+0.4	+0.87	+1.3	+0.08	+1.49

[a] In MeCN, vs SCE, at 25 °C unless otherwise indicated. [b] Voltammetric potential, Pt working electrode. [c] In DMF solution, Hg working electrode. [d] Excited-state energy estimated from the 77 K emission spectra. [f] Values in DMF/CH_2Cl_2 (9/1) 77 K glasses from ref 9 and 12.

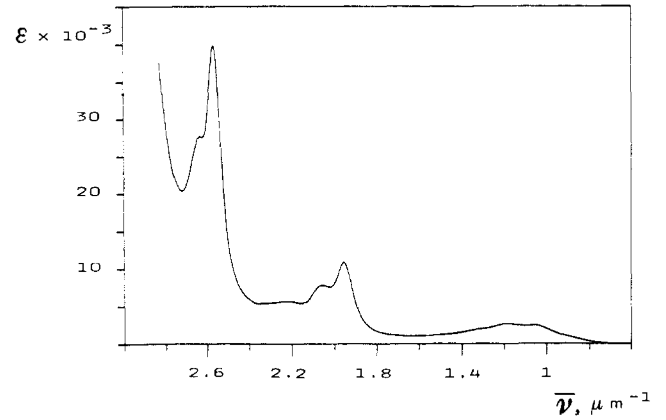

Figure 2. Absorption spectrum of $Ru(bpy)(CNMe)_4^+$ in acetonitrile.

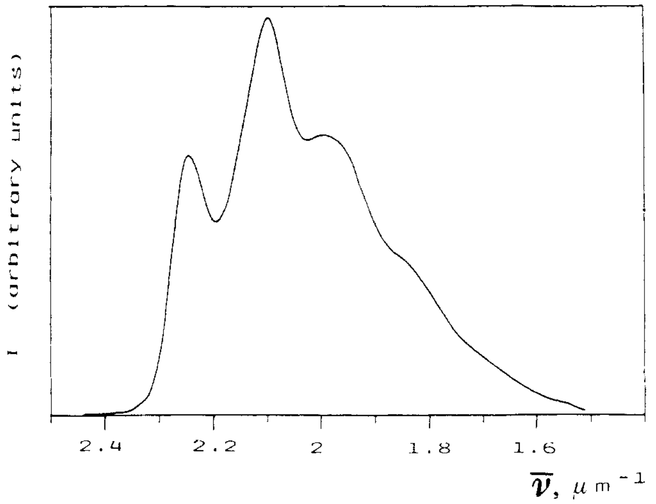

Figure 3. Room temperature emission spectrum of $Ru(bpy)(CNMe)_4^{2+}$ in aqueous solution.

are soluble in water and polar organic solvents (e.g., DMF and MeCN). In these solvents, the complexes are stable in the dark over long periods of time. They exhibit some sensitivity to near-UV light, which appears to cause release of methyl isocyanide ligands from the complexes. Their photosensitivity is comparable to that of other Ru(II) bipyridine complexes of photophysical interest (e.g., $\Phi \approx 10^{-4}$ at 313 nm for $Ru(bpy)(CNMe)_4^{2+}$ in water vs 7×10^{-5} at 436 nm for $Ru(bpy)_3^{2+}$[19]).

The spectra of the methyl isocyanide complexes in aqueous solution are shown in Figure 1, together with those of the parent cyanide compounds $Ru(bpy)_2(CN)_2$ and $Ru(bpy)(CN)_4^{2-}$. Absorption maxima for the lowest energy band in water and acetonitrile are also reported in Table I.

Methyl group resonances were observed in ^1H NMR at τ 6.54 for both $Ru(bpy)_2(CN)(CNMe)^+$ and $Ru(bpy)_2(CNMe)_2^{2+}$, and at τ 6.75 and τ 6.30 for $Ru(bpy)(CNMe)_4^{2+}$, in deuteriated MeCN. The IR spectra showed the following bands in the C–N stretching region: 2105, 2190 cm^{-1} for $Ru(bpy)_2(CN)(CNMe)^+$; 2185, 2205 cm^{-1} for $Ru(bpy)_2(CNMe)_2^{2+}$; 2220, 2260 cm^{-1} for $Ru(bpy)(CNMe)_4^{2+}$. These values are within the typical frequency ranges exhibited by ruthenium(II) complexes containing CN^- (2060 ± 50 cm^{-1})[2,20] and CNMe (2210 ± 50 cm^{-1})[2,18] ligands.

Redox Behavior. Cyclic voltammetry in MeCN solution was used to study the redox properties of the complexes. In the anodic range from 0 to +2.6 V vs SCE each of the complexes exhibited a single, appreciably reversible one-electron process that can be attributed to oxidation of the Ru(II) center. The half-wave potentials of this process, $E_{1/2}^{\text{ox}}$, are compared with those of the parent cyanide complexes in Table II. In the cathodic range from 0 to −1.9 V vs SCE both $Ru(bpy)_2(CN)(CNMe)^+$ and $Ru(bpy)_2(CNMe)_2^{2+}$ exhibited two appreciably reversible one-electron reduction processes (separated for both complexes by 0.190 V) that can be attributed to stepwise reduction of the two bpy ligands. Consistently, the $Ru(bpy)(CNMe)_4^{2+}$ complex only gave rise to a single reversible reduction process. The half-wave potentials, $E_{1/2}^{\text{red}}$, for the one-electron reduction of the bpy ligands in the three complexes are compared in Table II with the corresponding data for the parent cyanide complexes. As is usual for other bpy complexes,[21-23] irreversible waves corresponding to the second reduction process of the bpy ligands are observed at more negative potentials for all the complexes.

Electrolysis of deaerated acetonitrile solutions of $Ru(bpy)(CNMe)_4^{2+}$ in an OTTLE cell at −1.4 V vs Ag wire (see Experimental Section) produced the reduced form $Ru(bpy)(CNMe)_4^+$, with the spectrum shown in Figure 2. This species was not stable for periods longer than a few minutes, most probably because of substitution of isocyanide with solvent. The spectrum of $Ru(bpy)(CNMe)_4^+$ shown in Figure 2 has been put on a molar absorptivity scale by comparison with quantitative photochemical experiments to be described below.

Emission. In room temperature fluid solutions, $Ru(bpy)_2(CN)(CNMe)^+$ gave rise to a weak ($\Phi(H_2O) = 3 \times 10^{-4}$), broad, short-lived emission. Band maxima and lifetimes of this emission in water and MeCN are given in Table I. Under the same conditions, $Ru(bpy)_2(CNMe)_2^{2+}$ did not give rise to any appreciable luminescence. On the other hand, $Ru(bpy)(CNMe)_4^{2+}$ was found

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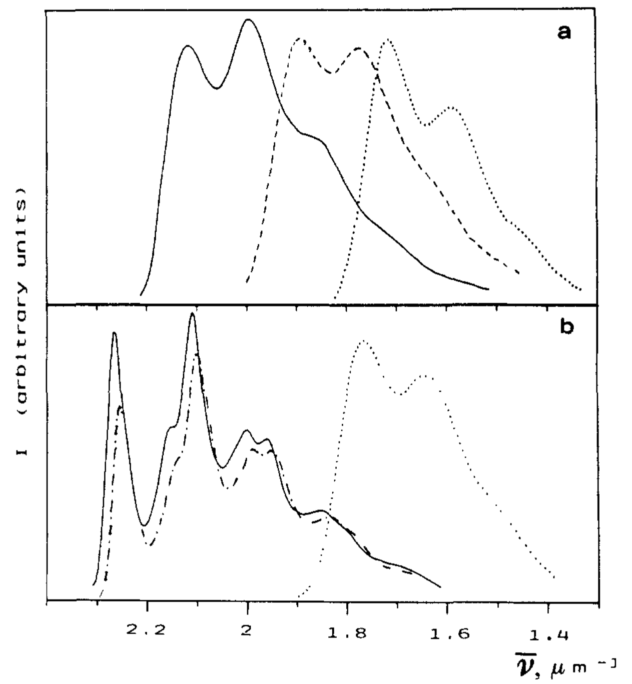

Figure 4. Low-temperature (77 K) emission spectra in absolute ethanol glass of (a) $Ru(bpy)_2(CN)_2$ (···), $Ru(bpy)_2(CN)(CNMe)^+$ (- - -), $Ru(bpy)_2(CNMe)_2^{2+}$ (—) and (b) $Ru(bpy)(CN)_4^{2-}$ (···), $Ru(bpy)(CNMe)_4^{2+}$ (—), $Rh(bpy)_3^{3+}$ (·-·).

Table III. Electron-Transfer Quenching of $^*Ru(bpy)(CNMe)_4^{2+}$ by Electron Donors (D)[a]

D	$E_{1/2}(D^+/D)$,[b] V	k_q, $M^{-1}\,s^{-1}$	k_b, $M^{-1}\,s^{-1}$	Φ_{ce}
1,4-dimethoxybenzene	1.34	5.3×10^9	3.8×10^9	0.5
1,2,3-trimethoxybenzene	1.42	1.4×10^9	3.2×10^9	0.5
1,3,5-trimethoxybenzene	1.49	9.3×10^7	6.3×10^9	0.2
triethylamine	0.96	3.8×10^9		1

[a] In MeCN solution, 0.02 M TEAP, 25 °C. [b] In MeCN, vs SCE, from: Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Non-Aqueous Systems*; Dekker: New York, 1970.

to luminesce strongly at room temperature in both water and MeCN. In deaerated aqueous solution, the quantum yield of this emission was 0.013. The corrected emission spectrum in aqueous solution is shown in Figure 3, and band maxima and lifetimes in the two solvents are given in Table I.

At 77 K in absolute ethanol glasses all the complexes emitted, although with different bandshapes and lifetimes. The emission spectra of $Ru(bpy)_2(CN)(CNMe)^+$ and $Ru(bpy)_2(CNMe)_2^{2+}$ are compared with that of the parent $Ru(bpy)_2(CN)_2$ in Figure 4a. The emission spectrum of $Ru(bpy)(CNMe)_4^{2+}$ is compared with those of the parent $Ru(bpy)(CN)_4^{2-}$ and of $Rh(bpy)_3^{3+}$ (see Discussion) in Figure 4b. Emission lifetimes at 77 K are given in Table I.

Laser photolysis of $Ru(bpy)(CNMe)_4^{2+}$ in aqueous or acetonitrile solutions gave rise to transient spectral changes that decayed with the same lifetime as the emission and can thus be assigned to excited-state absorption (ESA). The absolute ESA spectrum of $Ru(bpy)(CNMe)_4^{2+}$ shown in Figure 5 was obtained from laser experiments with actinometry,[12] making the usual assumption of unitary excited-state formation efficiency.[3]

Excited-State Quenching. Quenching experiments were carried out on the long-lived excited state of $Ru(bpy)(CNMe)_4^{2+}$ by using a number of electron donors as quenchers (Table III).

With triethylamine as electron donor (D) in MeCN, fast quenching of the excited state of $Ru(bpy)(CNMe)_4^{2+}$ was observed (Table III). The quenching occurred with a reductive electron-transfer mechanism (eq 1), as shown by the observation in laser photolysis of a product spectrum identical with that of Figure 2

$$^*Ru(bpy)(CNMe)_4^{2+} + D \xrightarrow{k_q} Ru(bpy)(CNMe)_4^{+} + D^+ \quad (1)$$

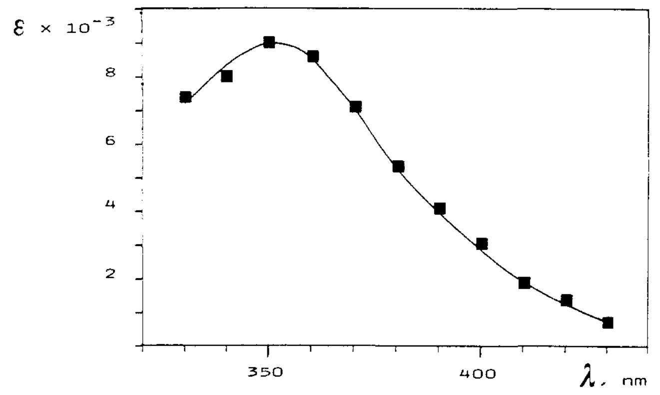

Figure 5. Excited-state absorption (ESA) spectrum of $Ru(bpy)(CNMe)_4^{2+}$ in aqueous solution.

(the oxidized amine does not absorb appreciably in the spectral range of interest). Molar absorptivity values for $Ru(bpy)(CNMe)_4^+$ (ϵ_{510nm}, 11 000 $M^{-1}\,cm^{-1}$) were obtained by quantitative scavenging of the primary reduced product by *N,N*-dimethyl-4,4′-bipyridine dication (methylviologen, MV^{2+})[24] (eq 2), using the known[25] molar absorptivity of the MV^+ formed. On the basis

$$Ru(bpy)(CNMe)_4^{+} + MV^{2+} \rightarrow Ru(bpy)(CNMe)_4^{2+} + MV^+ \quad (2)$$

of the molar absorptivity of $Ru(bpy)(CNMe)_4^+$, laser photolysis experiments with actinometry[12] gave a value of 1.0 ± 0.1 for the quantum yield, Φ_{ce}, of product formation (eq 1) at complete quenching. Stationary irradiation of deaerated MeCN solutions of $Ru(bpy)(CNMe)_4^{2+}$ and trimethylamine resulted in the accumulation of $Ru(bpy)(CNMe)_4^+$, showing that with this electron donor the photoinduced electron transfer (eq 1) is irreversible. This agrees with previous observations on electrochemical[26] and photochemical[27] oxidation of aliphatic amines.

Several methoxybenzenes were also used as electron donors (D) in MeCN. The quenching rate constants, k_q, are reported in Table III. The quenching was accompanied by transient formation of the expected redox products (eq 1).[28] The yields of redox products measured in laser photolysis, Φ_{ce}, were relatively high (Table III). With these electron donors in deaerated solution, the photoinduced electron transfer was fully reversible in the dark (eq 3). The back-electron transfer rate constants, k_b, are also reported in Table III.

$$Ru(bpy)(CNMe)_4^{+} + D^+ \xrightarrow{k_b} Ru(bpy)(CNMe)_4^{2+} + D \quad (3)$$

Discussion

Absorption Spectra. Large blue shifts in the Ru→bpy MLCT band are induced by substitution of cyanide with methyl isocyanide (Figure 1). For the $Ru(bpy)(CNMe)_4^{2+}$ complex, the shift is so large that the MLCT band is actually hidden by the ligand centered (LC) bands of bipyridine (Figure 1b). The blue shift reflects the decrease in electronic charge occurring on Ru(II) as a consequence of the higher π-acceptor ability and lower σ-donor ability of methyl isocyanide relative to cyanide.[16] It should be pointed out that spectral changes very similar to those shown in Figure 1 have been observed by protonation of the cyanide ligands of $Ru(bpy)_2(CN)_2$[11,14] and $Ru(bpy)(CN)_4^{2-}$[15] in concentrated H_2SO_4 solutions. From this point of view, methylation and

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[24] No appreciable quenching of $^*Ru(bpy)(CNMe)_4^{2+}$ by MV^{2+} occurred in this experiment.

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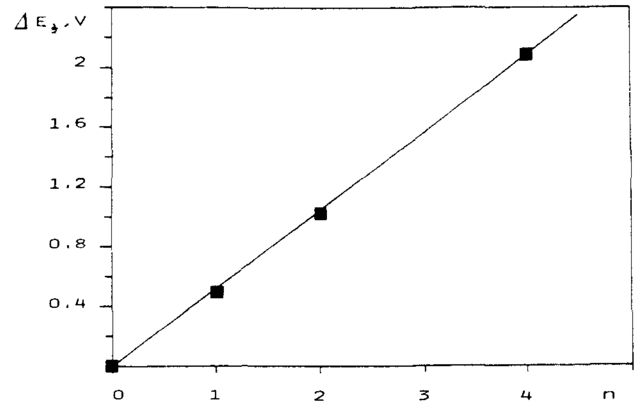

Figure 6. Plot of the shift in the oxidation potential obtained by substitution of cyanide with isocyanide, $E_{1/2}$, as a function of the number, n, of isocyanide ligands.

protonation of the cyanide ligands seem to have quite comparable consequences.

Substantial differences between the spectra of corresponding cyano and methyl isocyano complexes also show up in the UV region (see, in particular, Figure 1b). Although the presence in this region of MLCT states based on the isocyanide ligands cannot be definitely ruled out, these changes seem to be mainly determined by the sensitivity of the bpy-centered bands to the effective oxidation state of the metal. If the UV spectra of tris-bipyridyl complexes of a number of divalent (e.g., Fe(II), Ru(II), Os(II))[29] and trivalent (e.g. Cr(III),[30] Fe(III),[31] Ru(III),[17] Rh(III),[32] Os(III)[29]) metals are compared, an evident (though apparently previously unnoticed) regularity emerges: a structured absorption feature at ca. 320 nm is typical of LC absorption for bpy complexes with the trivalent (electron-poor, weakly back-bonding) metals, whereas a structureless band at ca. 280 nm is typical of complexes with divalent (electron-rich, strongly back-bonding) metals. Thus, in addition to the behavior of the MLCT bands, the evolution of the UV spectra in going from cyano to methyl isocyano complexes (Figure 1) also seems to reflect the strong electron-withdrawing effect of the isocyanide ligands. Again, it should be pointed out that the UV spectra of protonated cyanide complexes[15] are virtually identical with those of the corresponding methyl isocyanide species, confirming the substantial similarity of the two types of ligands.

Redox Behavior. An independent proof of the strong electron-withdrawing effect of the isocyanide ligands comes from the electrochemical results. Both in the bis- and in the mono-bpy series, substitution of cyanide with methyl isocyanide causes large anodic shifts in the potential for oxidation of the ruthenium center (Table II). The trend is a very regular one, as shown by Figure 6, in which the potential shifts with respect to the parent cyano complexes are plotted against the number of isocyanide ligands. It appears that a constant anodic shift of ca. 0.5 V is brought about by methylation of each cyanide ligand. In this connection, it can be recalled that $Ru(CNMe)_6^{2+}$ was reported[18] to be redox inactive up to +3 V (vs SCE), a seemingly striking figure for a Ru(II) complex. This, however, appears rather obvious in the light of the experimental trend of Figure 6, if reference is made to the parent $Ru(CN)_6^{4-}$ complex ($E_{1/2}^{ox}$ = +0.8 V in water vs NHE).[33] If the oxidation potential of $Ru(bpy)_3^{2+}$ ($E_{1/2}^{ox}$ = +1.24 in MeCN vs SCE)[3] is compared with those of $Ru(bpy)_2(CNMe)_2^{2+}$ and $Ru(bpy)(CNMe)_4^{2+}$ (Table II), it also appears that each substitution of one bpy ligand with two CNMe ligands shifts the potential anodically by ca 0.5 V. Thus, the electron-withdrawing effect of the three ligands toward Ru(II) seems to follow the order CNMe > (1/2)bpy > CN^-.

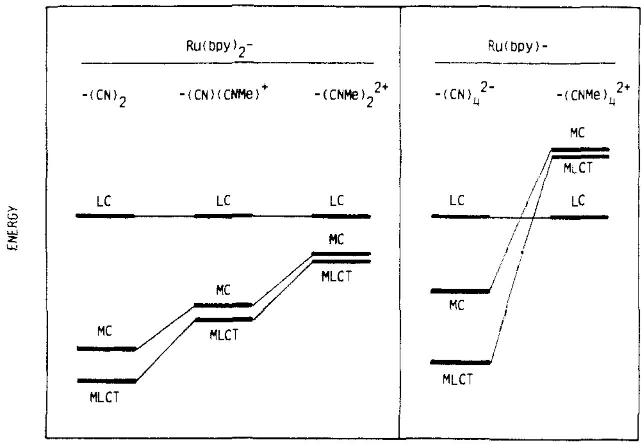

Figure 7. Schematic representation of the changes in the energy of the lowest excited states of the bis- and mono-bipyridine complexes induced by substitution of cyanide with isocyanide.

In polypyridine Ru(II) complexes, the low-energy reduction processes generally occur at the polypyridine ligands.[34] Consistent with this notion, the reduction potentials undergo a smaller overall variation within the series of complexes investigated (Table II) as compared to the oxidation potentials. The fact that the spectrum of $Ru(bpy)(CNMe)_4^+$ (Figure 2) is similar to that of $Ru(bpy)_3^+$,[35] clearly showing the bpy^- absorption features[36] at 2.56, 1.96, and 1.19 μm^{-1}, constitutes a direct proof that reduction occurs at the bpy ligand in this complex. Since reduction at the bpy ligand, as such, is not expected to affect appreciably the stability of the complex, the observed lability of $Ru(bpy)(CNMe)_4^+$ (see Results) could imply that thermally activated intramolecular electron transfer to the metal occurs with appreciable efficiency in this molecule.

Photophysical Behavior. The substitution of cyanide ligands with methyl isocyanide has interesting consequences on the excited-state behavior of the complexes, as shown by the low-temperature spectra of Figure 4. Generally speaking, methylation causes blue shifts in the emission, but the emission bandshape does not remain the same for all the complexes. For $Ru(bpy)_2(CN)_2$, $Ru(bpy)(CN)_4^{2-}$, $Ru(bpy)_2(CN)(CNMe)^+$, and $Ru(bpy)_2(CNMe)_2^{2+}$, the band profile is that of the typical LMCT low-temperature emission exhibited by Ru(II) bipyridine complexes:[37] discernible vibrational structure, broad individual vibrational components, single progression of ca. 0.13 μm^{-1}. The relative intensity of the 0–0, 0–1, 0–2, etc., vibrational components seems to reveal an increasing degree of distortion with increasing energy of the emission (Figure 4), a feature that might be related to an increasing amount of charge actually transferred to the bpy ligand. For $Ru(bpy)(CNMe)_4^{2+}$, on the other hand, the band profile is a completely different one: very evident vibrational structure, sharp, narrow individual vibrational components, two progressions of 0.159 μm^{-1} separated from each other by 0.046 μm^{-1}. This kind of emission is typical of a ligand-centered (LC) low-temperature emission.[38] The assignment is clearly borne out by the close matching of the $Ru(bpy)(CNMe)_4^{2+}$ emission with the well-established[38] LC emission of $Rh(bpy)_3^{3+}$ (Figure 4b). The very long low-temperature lifetime of $Ru(bpy)(CNMe)_4^{2+}$ relative to the other complexes (Table I) corroborates the LC assignment. Again, it should be pointed out that low-temperature emission spectra and lifetimes very similar to those of $Ru(bpy)_2(CNMe)_2^{2+}$ and $Ru(bpy)(CNMe)_4^{2+}$ can be obtained by protonation of $Ru(bpy)_2(CN)_2$[11] and $Ru(bpy)(CN)_4^{2-}$,[15] respectively, in concentrated sulfuric acid.

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The change in the nature of the lowest excited state obtained upon substitution of cyanide with methyl isocyanide in the mono-bpy complex is an extreme example of "tuning" of the photophysical properties of a complex by modifications in nonchromophoric ligands. This arises because of the high sensitivity of MLCT states on one hand, and the much lower sensitivity of LC states on the other, to the electron donor and acceptor power of the ancillary ligands, as shown schematically in Figure 7. In the case of the two mono-bpy complexes the blue shift in the MLCT state is so large as to cause complete inversion between MLCT and LC states.

The photophysical behavior in room temperature fluid solutions is difficult to analyze in detail. In fact, for Ru(II) polypyridine complexes thermally activated decay pathways going through short-lived MC states have to be taken into consideration.[5-7,39] Therefore, a complete picture of the energy shifts of the LC, MLCT, *and* MC states upon substitution of cyanide with methyl isocyanide would be needed. In principle, methyl isocyanide is a better π-acceptor and a poorer σ-donor than cyanide.[16] The two effects are expected to cooperate in withdrawing charge from Ru(II) thus increasing the energy of the MLCT states, but they should oppose each other as far as the energy of the MC states is concerned. Therefore, the absolute energy of the MC states will increase or decrease by substitution of cyanide with methyl isocyanide depending on whether π-bonding or σ-bonding effects predominate.

For $\mathrm{Ru(bpy)(CNMe)_4}^{2+}$, a structured emission very similar to that observed at low temperature is also obtained in room temperature fluid solutions (Figure 3). The fact that the excited state populated at room temperature is LC rather than MLCT in character is also demonstrated by the ESA spectrum (Figure 5), which is completely different from the typical spectra of MLCT excited states.[9,40,41] The lifetime in these conditions is remarkably long, indicating that the lowest LC state is energetically well isolated from (i.e., at least 0.2 μm^{-1} lower than) upper short-lived MC states.[42-44] Although the exact energy of the MC states in the parent cyano complex is not known, this result seems to indicate that substitution of cyanide with methyl isocyanide brings about an *increase* in the energy of the MC states, implying that changes in π-bonding strength predominate over those in σ-bonding. Such a situation is schematically depicted in Figure 7.

In the $\mathrm{Ru(bpy)_2(CN)_2}$, $\mathrm{Ru(bpy)_2(CN)(CNMe)}^{+}$, $\mathrm{Ru(bpy)_2(CNMe)_2}^{2+}$ series, the MLCT emission lifetime decreases considerably in going from the first to the second complex, and virtually no emission can be detected for the last complex. This is most probably due to the different sensitivity of MLCT and MC states to substitution: the slower increase in energy of the MC state lowers the energy gap, allowing fast activated decay of the MLCT state to occur. Such a situation is schematically depicted in Figure 7.[45]

Excited-State Redox Behavior. The excited-state redox potentials, calculated from electrochemical potentials and excitation energies according to standard procedures,[46] are given in Table II for the various complexes. Generally speaking, substitution of cyanide with isocyanide causes an increase in the oxidizing power and a decrease in the reducing power of the excited state. This effect leads to quite remarkable excited-state redox properties in the case of $\mathrm{Ru(bpy)(CNMe)_4}^{2+}$. In fact, excited Ru(II) polypyridine complexes are typically good reductants and mild oxidants.[1-3] On the contrary, $\mathrm{Ru(bpy)(CNMe)_4}^{2+}$ is expected to behave as a strong photochemical *oxidant* ($*E_{1/2}$, +1.49 V vs SCE) and as a very poor reductant. This expectation is quantitatively borne out by the quenching rate constants obtained with methoxybenzenes of increasing oxidation potential: the sharp inflection obtained between +1.42 and +1.49 V (vs SCE) is the typical behavior predicted by standard electron transfer models for reactions with small reorganizational energies near to the isoergonic threshold.[27,46]

From the point of view of the excited-state redox properties, $\mathrm{Ru(bpy)(CNMe)_4}^{2+}$ resembles polypyridine complexes of trivalent metals such as $\mathrm{Cr(bpy)_3}^{3+}$ ($*E_{1/2}$, 1.45 V vs SCE)[27,47] and $\mathrm{Rh(phen)_3}^{3+}$ ($*E_{1/2}$, 2.0 V vs SCE).[44,48] Such complexes have potential applications in photochemical oxidation reactions of practical interest. In principle, the Rh(III) complexes are better than the Cr(III) ones not only for their higher oxidizing power but because they usually give rise to higher yields of primary products escaping the solvent cage.[48] Both the Cr(III) and Rh(III) photochemical oxidants, however, suffer from the lability of their one-electron reduced forms,[47,49] a feature that constitutes a severe limitation for their practical use in cyclic photocatalytic reactions. As a photochemical oxidant, $\mathrm{Ru(bpy)(CNMe)_4}^{2+}$ is similar to Cr(III) polypyridine complexes in the oxidizing power and to Rh(III) polypyridine complexes in cage escape yields (Table III). Contrary to the expectations (see above) based on the site of reduction, however, its stability in the reduced state is no better than that of the Cr(III) and Rh(III) photosensitizers. The search for transition-metal-based photochemical oxidants suitable for cyclic use seems thus to remain a challenging but elusive task.

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