greater repulsive forces. In any event, it will be worthwhile to examine some additional edge-sharing bioctahedral complexes in the earliest and in the later columns to see if the pattern of M–M bonding for the former and no M–M bonding for the latter persists in a general way.

Acknowledgment. We thank Dr. K. Vidyasager for help with the crystallography and the National Science Foundation for support.

Supplementary Material Available: Tables of positional parameters, anisotropic displacement parameters, and additional bond distances and angles and additional drawings for **1**, **3**, and **4** (25 pages); listings of calculated and observed structure factors (41 pages). Ordering information is given on any current masthead page.

Contribution from the Institut für Anorganische Chemie,
Universität Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80, West Germany

Energy Level Tailoring in Ruthenium(II) Polyazine Complexes Based on Calculated and Experimental Ligand Properties

Sylvia D. Ernst[1] and Wolfgang Kaim*

Received October 5, 1988

The effects of experimental and calculated ligand properties on the electronic structure of ruthenium(II) polyazines have been rationalized in the complexes $(L_3Ru)^{2+}$, $[(L)Ru(bpy)_2]^{2+}$, and $\{(\eta^4,\mu\text{-}L)[Ru(bpy)_2]_2\}^{4+}$, where L denotes the four isomeric bidiazines 3,3′-bipyridazine, 2,2′-bipyrazine, and 2,2′- and 4,4′-bipyrimidine and η^2-azo-2,2′-bipyridine and where η^4,μ-L denotes the symmetrically bridging ligands 2,2′-bipyrimidine, 2,5-bis(2-pyridyl)pyrazine, 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, and azo-2,2′-bipyridine. Crucial factors determining the redox potentials and metal-to-ligand charge-transfer (MLCT, d → π^*) absorption energies are the ground-state basicities, the π^* orbital energies, and electron densities at the coordinating atoms of the ligands. Mono- and binuclear complexes with unusually long wavelength MLCT absorptions have been obtained by applying the described strategies in the design and selection of ligands.

Introduction

The intensely colored $[Fe(bpy)_3]^{2+}$ ion (bpy = 2,2′-bipyridine), first observed more than a century ago[2] and of great analytical value,[3,4] has found its modern pendant in the homologous $[Ru(bpy)_3]^{2+}$ ion, a complex with outstanding and much investigated[5-7] photophysical and photochemical properties. Recent comprehensive reviews[5] illustrate the widespread use of this complex and of its derivatives in electron- and energy-transfer reactions. In view of the vast body of data,[5] a more selective approach toward such new compounds seems appropriate, a rational design of ligands that convey desired properties such as absorption energies and redox potentials to the complexes.

Chart I

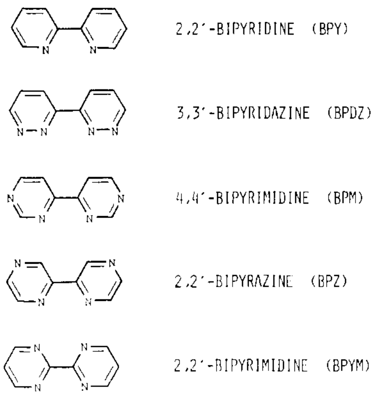
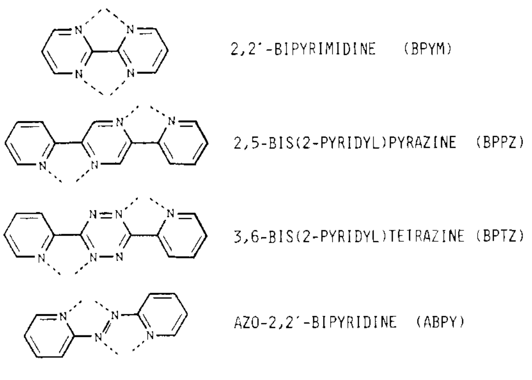


Chart II



Employing two series of deliberately selected mono- and binucleating polyazine chelate ligands (Charts I and II),[8,9] we now present complete sets of electrochemical and optical absorption data for ruthenium(II) complexes (Chart III) and correlate the experimental information with recently published results from Hückel perturbation calculations for the π ligands.[8b,9b]

Chart III

$$(L_3Ru)^{2+} \qquad [(L)Ru(bpy)_2]^{2+}$$

L = bpy, bpdz, bpm, bpz, bpym, abpy

$$\{(\eta^4,\text{-}\mu\text{-}L)[Ru(bpy)_2]_2\}^{4+}$$

η^4,μ-L = bppym, bppz, bptz, abpy

---

(1) Present address: Beilstein-Institut Für Organische Chemie, D-6000 Frankfurt/Main, West Germany.

(2) Blau, F. *Ber. Dtsch. Chem. Ges.* **1888**, *21*, 1077.

(3) Schilt, A. A. *Applications of 1,10-Phenanthroline and Related Compounds*; Pergamon: London, 1969.

(4) McWhinnie, W. R.; Miller, J. F. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 135.

(5) (a) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (b) Krause, R. A. *Struct. Bonding* **1987**, *67*, 1. (c) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(6) (a) Braterman, P. S.; Heath, G. A.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1801. (b) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3967. (c) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3877. (d) Braterman, P. S. *Inorg. Chem.* **1986**, *25*, 1732. (e) Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1987**, *109*, 7613. (f) Yersin, H.; Gallhuber, E.; Hensler, G. *Chem. Phys. Lett.* **1987**, *134*, 497.

(7) (a) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441. (b) Carlin, C. M.; DeArmond, M. K. *Chem. Phys. Lett.* **1982**, *89*, 297. (c) McClanahan, S. F.; Dallinger, R. F.; Holler, R. J.; Kincaid, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4853. (d) Ferguson, J.; Krausz, E. *Inorg. Chem.* **1986**, *25*, 3333. (e) Ferguson, J.; Krausz, E.; Vrbanicich, J. *Chem. Phys. Lett.* **1986**, *131*, 463. (f) Ferguson, J.; Krausz, E. *Inorg. Chem.* **1987**, *26*, 1383. (g) Myrick, M. L.; Blakley, R. L.; DeArmond, M. K. *J. Am. Chem. Soc.* **1987**, *109*, 2841. (h) Myrick, M. L.; Blakley, R. L.; DeArmond, M. K.; Arthur, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 1325.

(8) (a) Ernst, S.; Kaim, W. *Angew. Chem.* **1985**, *97*, 431; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 430. (b) Ernst, S.; Kaim, W. *J. Am. Chem. Soc.* **1986**, *108*, 3578. (c) Ernst, S.; Kohlmann, S.; Kaim, W. *J. Organomet. Chem.* **1988**, *354*, 177.

(9) (a) Kohlmann, S.; Ernst, S.; Kaim, W. *Angew. Chem.* **1985**, *97*, 698; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 684. (b) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1987**, *26*, 68.

0020-1669/89/1328-1520$01.50/0 © 1989 American Chemical Society

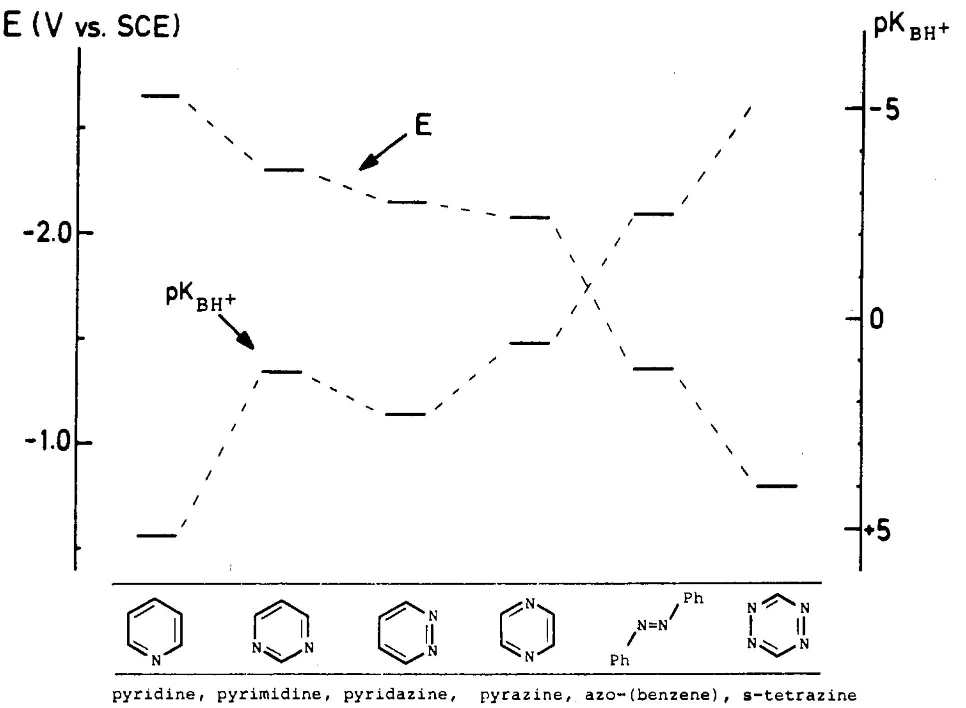
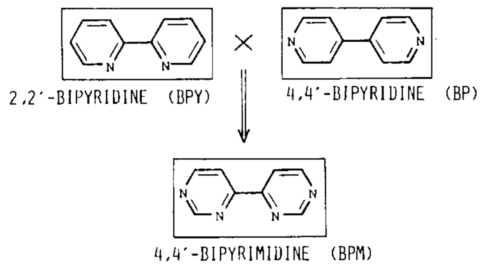


Figure 1. σ-donor vs π-acceptor properties of components of nitrogen chelate ligands as illustrated by pK_{BH^+} values[18] and reduction potentials.[19]

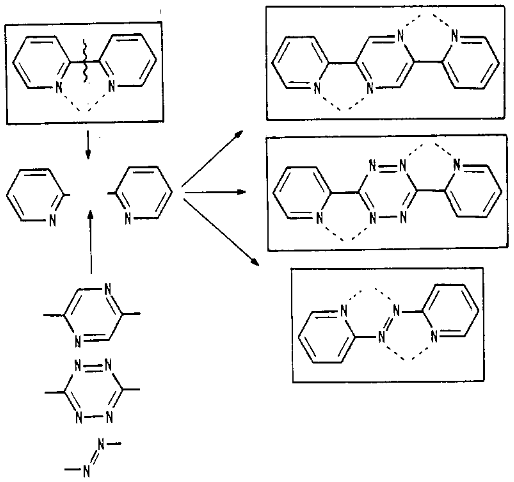
Chart IV



Ligand Selection. The century-old[2] 2,2'-bipyridine molecule, the "*E. coli* of coordination chemistry",[10] is the starting system for rational ligand modification. Maintaining at least C_{2v} symmetry and the α-diimine chelate arrangement, the replacement of one CH group in each pyridine ring by a more electronegative nitrogen atom leads to the series of the four *isomeric* and *isonodal* bidiazines given in Charts I and V. These ligands have been characterized in comparative studies of group 6 metal tetracarbonyl complexes;[8b,c] bpdz is the most basic isomer,[11] whereas bpm, the "hybrid" between 2,2'- and 4,4'-bipyridine (Chart IV), possesses the lowest lying π* level (Chart V).[8]

In another hybridization procedure (Scheme I) the bpy system is cut in half and a bifunctional, π-electron-deficient yet σ-coordinating fragment is inserted. This strategy produces strong π-acceptor ligands[9] that, like the bidiazine isomer bpym,[12] can act as symmetrically bis-chelating molecular bridges between metal centers. In this paper we correlate data for known complexes[12-16] and our own results for deliberately selected new compounds with the ligand properties.[8,9]

Scheme I



Ruthenium(II) is renowned for forming very inert bonds with imine nitrogen centers,[17] and the ligand σ-donor strength as estimated by the protonation constant, pK_{BH^+},[18] does play an important role in determining the energy of occupied metal d levels and the potential for dissociation. On the other hand, the accessibility of a redox-active metal-to-ligand charge-transfer (MLCT) excited state at low energy depends on the presence of low-lying π* levels in the coordinated ligand(s). A look at the set of ligand fragments (Figure 1) from which the chelating molecules in Charts I and II have been constructed shows a dilemma: The ligand σ-donor strength as illustrated by the pK_{BH^+}

---

(10) Lehn, J. M. Lecture at the 1st European Inorganic Chemistry Seminar, Dourdan, France, 1988.

(11) Ernst, S.; Kaim, W. *Inorg. Chim. Acta* **1986**, *114*, 123.

(12) (a) Hunziker, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7370. (b) Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660.

(13) (a) Crutchley, R. J.; Lever, A. B. P. *J. Am. Chem. Soc.* **1980**, *102*, 7128. (b) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617. (c) Tait, C. D.; Donohoe, R. J.; DeArmond, M. K.; Wertz, D. W. *Inorg. Chem.* **1987**, *26*, 2754.

(14) (a) Kitamura, N.; Kawanishi, Y.; Tazuke, S. *Chem. Lett.* **1983**, 1185. (b) Kitamura, N.; Kawanishi, Y.; Tazuke, S. *Chem. Phys. Lett.* **1983**, *97*, 103. (c) Tazuke, S.; Kitamura, N. *Pure Appl. Chem.* **1984**, *56*, 1269. (d) Tazuke, S.; Kitamura, N.; Kim, H. B. In *Photochemical Energy Conversion*; Norris, J. R., Jr., Meisel, D., Eds.; Elsevier: Amsterdam, 1989.

(15) Rillema, D. P.; Mack, K. B. *Inorg. Chem.* **1982**, *21*, 3849.

(16) Dürr, H.; Dörr, G.; Zengerle, K.; Mayer, E.; Curchod, J.-M.; Braun, A. M. *Nouv. J. Chim.* **1985**, *9*, 717.

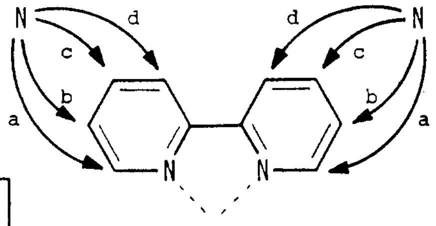
(17) Taube, H. *Angew. Chem.* **1984**, *96*, 315; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 329.

(18) (a) Perrin, F. F. *Dissociation Constants of Organic Bases in Aqueous Solutions*; Butterworths: London, 1965. (b) Stewart, R. *The Proton in Applications to Organic Chemistry*; Academic Press: New York, 1985. (c) Spanget-Larsen, J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 417.

(19) Meites, L., Zumann, P., Eds. *Handbook Series in Organic Electrochemistry*; CRC Press: Boca Raton, FL, 1977–1982; Vol. I–V.

Chart V

THE BIDIAZINES

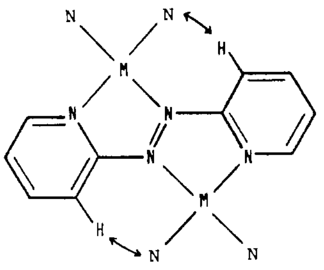


basicity:		reduction potential: (DMF)
pK_{BH^+} = 3.37	a : 3,3'-bipyridazine (bpdz)	- 1.72 V vs. SCE
pK_{BH^+} = 1.5	b : 4,4'-bipyrimidine (bpm)	- 1.34 V "
pK_{BH^+} = 0.45	c : 2,2'-bipyrazine (bpz)	- 1.59 V "
	d : 2,2'-bipyrimidine (bpym)	- 1.73 V "

values decreases in about the same fashion as the ligand π^* levels become more accessible, indicated here by increasing reduction potentials. While the former effect causes a stabilization of filled metal d orbitals, the latter effect leads to a stabilization of ligand-centered LUMOs available for charge transfer and the net result for the energy of the charge-transfer transition may be negligible as shown later in Figures 4 and 5.

Strategies to overcome such a situation, i.e. to shift the absorption maximum to lower energies, are desirable because there is a need for effective photocatalysts in the long-wavelength region of the solar spectrum.[20] Previous attempts have made use of substituent effects,[21,22] of extensions of the ligand π system,[23,24] and of polynucleating ligands;[15,25] we now present results of a calculation-guided approach toward the design of π-acceptor ligands.[26]

Chart VI



Energy correlation diagrams for the unoccupied π orbitals of the ligands in Charts I and II and electron densities (squared π MO coefficients) at the coordinating nitrogen centers have been published.[8,9b] Ruthenium has the advantage of dissociative stability when bonded to N in the +II (d^6) *and* +III (d^5) oxidation states,[17] which allows us to determine reliable potentials for the metal-centered oxidation. This also permits a correlation (eq 1) between

$$E_{\text{op}}\ (\text{eV}) = [(E_{\text{ox}} - E_{\text{red}})\ (\text{V})] + \chi \qquad (1)$$

energy data from electrochemical and electronic absorption experiments,[27] where χ comprises Franck–Condon contributions from intra- and intermolecular reorganization, including changes in solvation. On the other hand, complicating structural isomerism can occur in tris(α-diimine)ruthenium complexes,[28-30] and the

---

(20) (a) Bolton, J. R. *Science* **1978**, *202*, 705. (b) Adamson, A. W.; Namnath, J.; Shastry, V. J.; Slawson, V. *J. Chem. Educ.* **1984**, *61*, 221.

(21) (a) Elliott, C. M.; *J. Chem. Soc., Chem. Commun.* **1980**, 261. (b) Elliott, C. M.; Hershenhart, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 7519. (c) Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Skarda, V.; Thomson, A. J.; Glasper, J. L.; Robbins, D. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1303. (d) Skarda, V.; Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Thomson, A. J.; Robbins, D. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1309. (e) Ohsawa, Y.; Whangbo, M.-H.; Hanck, K. W.; DeArmond, M. K. *Inorg. Chem.* **1984**, *23*, 3426. (f) Alford, P. C.; Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Skarda, V.; Thomson, A. J.; Glasper, J. L.; Robbins, D. J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 705. (g) Wacholtz, W. F.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* **1986**, *25*, 227.

(22) Weiner, M. A.; Basu, A. *Inorg. Chem.* **1980**, *19*, 2797.

(23) (a) Klassen, D. M. *Inorg. Chem.* **1976**, *15*, 3166. (b) Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1981**, *64*, 275. (c) Ackermann, M. N.; Interrante, L. V. *Inorg. Chem.* **1984**, *23*, 3904. (d) Chambron, J. C.; Sauvage, J. P.; Amouyal, E.; Koffi, P. *Nouv. J. Chim.* **1985**, *9*, 527. (e) Thummel, R. P.; Lefoulon, F. *Inorg. Chem.* **1987**, *26*, 675. (f) Pyle, A. M.; Barton, J. K. *Inorg. Chem.* **1987**, *26*, 3820.

(24) (a) Krause, R. A.; Krause, K. *Inorg. Chem.* **1982**, *21*, 1714. (b) Gosh, P.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1985**, 361. (c) Krause, R. A.; Krause, K. *Inorg. Chem.* **1984**, *23*, 2195. (d) Wolfgang, S.; Strekas, T. C.; Gafney, H. D.; Krause, R. A.; Krause, K. *Inorg. Chem.* **1984**, *23*, 2650.

(25) (a) Rillema, D. P.; Callahan, R. W.; Mack, K. B. *Inorg. Chem.* **1982**, *21*, 2589. (b) Braunstein, C. H.; Baker, A. D.; Strekas, T. C.; Gafney, H. D. *Inorg. Chem.* **1984**, *23*, 857. (c) Gisselbrecht, J.-P.; Gross, M.; Lehn, J.-M.; Sauvage, J.-P.; Ziessel, R.; Piccinni-Leopardi, C.; Arrieta, J. M.; Germain, G.; Van Merssche, M. *Nouv. J. Chim.* **1984**, *8*, 659. (d) Fuchs, Y.; Lofters, S.; Dieter, T.; Shi, W.; Morgans, R.; Strekas, T. C.; Gafney, H. D.; Baker, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 2691. (e) Masschelein, A.; Kirsch-DeMesmaeker, A.; Verhoeven, C.; Nasielski-Hinkens, R. *Inorg. Chim. Acta* **1987**, *129*, L13. (f) Sahai, R.; Morgan, L.; Rillema, D. P. *Inorg. Chem.* **1988**, *27*, 3495. (g) Thummel, R. P.; Hery, C.; Williamson, D.; Lefoulon, F. *J. Am. Chem. Soc.* **1988**, *110*, 7894. (h) Akasheh, T. S.; El-Ahmed, Z. M. *Chem. Phys. Lett.* **1988**, *152*, 414. (i) Cf. also: Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1988**, *71*, 1511. (j) Murphy, W. R., Jr.; Brewer, K. J.; Gettliffe, G.; Petersen, J. D. *Inorg. Chem.* **1989**, *28*, 81.

(26) For previous, less systematic approaches cf.: (a) Ford, P. C. *Rev. Chem. Intermed.* **1979**, 267. (b) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4803. (c) Henderson, L. J., Jr.; Fronczek, F. R.; Cherry, W. R. *J. Am. Chem. Soc.* **1984**, *106*, 5876. (d) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613. (e) Wacholtz, W. M.; Auerbach, R. A.; Schmehl, R. H.; Ollino, M.; Cherry, W. R. *Inorg. Chem.* **1985**, *24*, 1758. (f) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 106. (g) Petersen, J. D.; Murphy, W. R.; Sahai, R.; Brewer, K. J.; Ruminski, R. R. *Coord. Chem. Rev.* **1985**, *64*, 26. (h) Brewer, K. J.; Murphy, W. R., Jr.; Spurlin, S. R.; Petersen, J. D. *Inorg. Chem.* **1986**, *25*, 882. (i) Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 4115. (j) Os analogues: Johnson, S. R.; Westmoreland, T. D.; Caspar, J. V.; Barqawi, K. R.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 3195. (k) Johnson, S. R.; Westmoreland, T. D.; Caspar, J. V.; Barqawi, K. R. *Inorg. Chem.* **1988**, *27*, 3195. (l) Juris, A.; Campagna, S.; Balzani, V.; Gremaud, G.; von Zelewsky, A. *Inorg. Chem.* **1988**, *27*, 3652. (m) Barqawi, K. R.; Llobet, A.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7751.

(27) (a) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984. (b) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1985**, *119*, 61; **1986**, *124*, 152.

(28) (a) Rillema, D. P.; Jones, D. S.; Levy, H. A. *J. Chem. Soc., Chem. Commun.* **1979**, 849. (b) Egglestone, D. S.; Goldsby, A.; Hodgson, D. J.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 4573. (c) Barton, J. K.; Goldberg, J. M.; Kumar, C. V.; Turro, N. J. *J. Am. Chem. Soc.* **1986**, *18*, 2081. (d) Goldstein, B. M.; Barton, J. K.; Berman, H. M. *Inorg. Chem.* **1986**, *25*, 842.

interaction between π ligands,[31] especially in charge-transfer excited states, has given rise to much debate, even for the simple $[Ru(bpy)_3]^{2+}$ system.[6,7]

Experimental Section

Physical Measurements. ^1H NMR spectra were obtained by using a Bruker WH 270 system and deuterated acetonitrile. UV–vis–near-IR spectra were recorded on Pye-Unicam SP 1800 and Perkin-Elmer Lambda 9 spectrophotometers in Spectrograde CH_3CN. Cyclic voltammetry was performed by using a PAR 363 potentiostat and Bank VSG 72 function generator. The electrochemical cell contained a three-electrode arrangement, a saturated calomel reference electrode (SCE), a Pt counter electrode, and a glassy-carbon working electrode. A 0.1 M solution of recrystallized and rigorously dried n-$Bu_4N^+ClO_4^-$ in dry, oxygen-free acetonitrile was used as electrolyte.

Preparation of Compounds. The ligands bpdz,[32] bpm,[33] bppz,[34] bptz,[35] and abpy[36] and the complex $RuCl_2(DMSO)_4$[37] (DMSO = dimethyl sulfoxide) were synthesized according to previously published procedures. All other starting materials were commercially available. We have already reported the syntheses, some NMR data, and elemental analyses of the compounds $[Ru(bpm)_3](PF_6)_2$,[8a] $[Ru(bpm)(bpy)_2](PF_6)_2$,[8a] $\{(\mu\text{-bppz})[Ru(bpy)_2]_2\}(PF_6)_4$,[30] $\{(\mu\text{-bptz})[Ru(bpy)_2]_2\}(PF_6)_4$,[9a,38] and $\{(\mu\text{-abpy})[Ru(bpy)_2]_2\}(PF_6)_4$.[9a,30]

$[Ru(abpy)_3](PF_6)_2$. A 175-mg (0.95-mmol) amount of azo-2,2′-bipyridine and 100 mg (0.20 mmol) of $RuCl_2(DMSO)_4$ were heated under reflux in ethanol/water (10:1.5) for 20 min. A 10-mL portion of a saturated solution of NH_4PF_6 in water was added; further addition of water yielded the red product, which was recrystallized from acetonitrile/diethyl ether (1:1) to yield 120 mg (64%).

$[Ru(bpdz)(bpy)_2](PF_6)_2\cdot H_2O$. A 135-mg (0.85-mmol) amount of 3,3′-bipyridazine and 180 mg (0.35 mmol) of $Ru(bpy)_2Cl_2\cdot 2H_2O$ were heated under an argon atmosphere in ethylene glycol for $^1/_2$ h. The cooled reaction mixture was treated with 3 mL of a saturated solution of NH_4PF_6 in water, and more water was added until a brownish yellow material precipitated. Column chromatography on acetonitrile/alumina (Woelm A, Super I, W 200) gave an orange-brown solution as the main fraction. Precipitation with diethyl ether yielded 145 mg (48%) of the monohydrate. Anal. Calcd for $C_{28}H_{24}F_{12}N_8OP_2Ru$ (M_r = 861.55): C, 38.23; H, 2.75; N, 12.74. Found: C, 38.98; H, 2.85; N, 12.85. ^1H NMR (CD_3CN): bpdz ligand, δ 8.63 (dd, 1.7, 8.7 Hz, 2 H, H(4)), 7.86 (dd, 5.1, 8.7 Hz, 2 H, H(5)), 8.95 (dd, 1.7, 5.1 Hz, 2 H, H(6)); bpy ligands, δ 8.46 (d, 8 Hz, 4 H, H(3,3′)), 8.06, 8.07 (m, 4 H, H(4,4′)), 7.38, 7.40 (m, 4 H, H(5,5′)), 7.60 (d, 5.3 Hz, 2 H, H(6)), 7.73 (d, 5.3 Hz, 2 H, H(6′)).

$[Ru(abpy)(bpy)_2](PF_6)_2\cdot C_2H_5OH$. A 200-mg (1.10-mmol) amount of azo-2,2′-bipyridine and 570 mg (1.11 mmol) of $Ru(bpy)_2Cl_2\cdot 2H_2O$ were heated for 1 h in argon-saturated ethanol/water (1:5). Addition of a saturated solution of NH_4PF_6 in water results in the precipitation of 350 mg (34%) of the red product. Anal. Calcd for $C_{32}H_{30}F_{12}N_8OP_2Ru$ (M_r = 935.58): C, 41.13; H, 3.24; N, 11.99. Found: C, 41.16; H, 3.30; N, 11.49.

Results

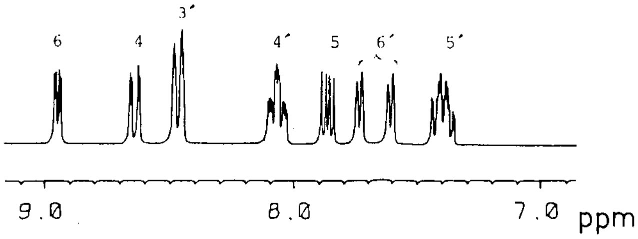


Figure 2. ^1H NMR spectrum of $[(bpdz)Ru(bpy)_2](PF_6)_2$ in CD_3CN. Primed positions refer to the bpy ring system.

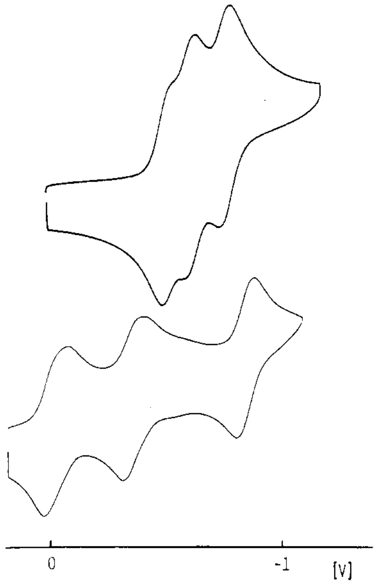


Figure 3. Cyclic voltammograms for the first three one-electron-reduction steps of $[Ru(bpm)_3]^{2+}$ (top) and $[Ru(abpy)_3]^{2+}$ (bottom) in acetonitrile.

Formation and Structure of Mono- and Binuclear Complexes. Most bis chelate π-acceptor ligands form binuclear complexes very readily because of the previously noted[39,40] phenomenon of "charge transfer assisted polynucleation": Coordination of a first back-donating metal fragment increases the basicity of the remaining donor atoms so as to enhance a second coordination.

An exception to this rule is the abpy system:[9,41,42] Nonbonded interactions (Chart VI) occur between the protons H(6,6′) and equatorial ligands at the octahedral metal centers, causing unusual NMR shifts and a notable activation barrier for the formation of such species from mononuclear precursors.[9b] Similarly, the mononuclear complex in the abpy/$[Ru(bpy)_2]^{2+}$ system is quite persistent and can be converted to the binuclear complex only after additional thermal activation.[30] The abpy ligand is thus suitable to form a tris(ligand) complex that is related to the 2-(phenylazo)pyridine species reported before;[24] the other binucleating ligands instead use both chelating sites and form coordination polymers with Ru^{2+}.

Structural isomerism in tris(chelate)ruthenium complexes has been outlined before.[5,24,28-30] Three C_{2v} symmetrical ligands give rise to enantiomers due to the chirality of the metal center; three identical unsymmetrical chelate ligands such as abpy may lead to *fac* and *mer* diastereoisomers.[24] In agreement with the argumentation for 2-(phenylazo)pyridine systems[24] we assume that the *mer* isomer is predominantly formed; an NMR analysis has not been possible because of the overlap of signals from numerous different 2-pyridyl groups in the 7 ppm < δ < 9 ppm region.[29,30] The mononuclear complexes $[Ru(bdz)(bpy)_2]^{2+}$ show NMR spectra that are more readily interpreted, as shown for the new bpdz derivative (Figure 2). There are the splitting patterns of the bidiazine ligand and of two slightly different "axial" and "equatorial" 2-pyridyl groups of the bpy ligands; the largest

---

(29) (a) Anderson, M. A.; Richards, J. P. G.; Stark, A. G.; Stephens, F. S.; Vagg, R. S.; Williams, P. A. *Inorg. Chem.* **1986**, *25*, 4847. (b) Orellana, G.; Alvarez Ibarra, C.; Santoro, J. *Inorg. Chem.* **1988**, *27*, 181.

(30) Ernst, S.; Kasack, V.; Kaim, W. *Inorg. Chem.* **1988**, *27*, 1146.

(31) (a) Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *Chem. Phys. Lett.* **1982**, *92*, 646. (b) Braterman, P. S.; Harriman, A.; Heath, G. A.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1801.

(32) Lafferty, J. J.; Case, F. H. *J. Org. Chem.* **1967**, *32*, 1591.

(33) Effenberger, F. *Chem. Ber.* **1965**, *98*, 2260.

(34) Case, F. H.; Loft, E. *J. Am. Chem. Soc.* **1959**, *81*, 905.

(35) Gelhard, J. F.; Lions, F. *J. Org. Chem.* **1965**, *30*, 318.

(36) Kirpal, A.; Reiter, L. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 664.

(37) Evans, J. P.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.

(38) (a) Kaim, W.; Ernst, S.; Kohlmann, S.; Welkerling, P. *Chem. Phys. Lett.* **1985**, *118*, 431. (b) Jaradat, Q.; Barqawi, K.; Akasheh, T. S. *Inorg. Chim. Acta* **1986**, *116*, 63.

(39) (a) Ernst, S.; Kaim, W. *Inorg. Chim. Acta* **1988**, *144*, 223. (b) Kaim, W.; Olbrich-Deussner, B.; Gross, R.; Ernst, S.; Kohlmann, S.; Bessenbacher, C. *Importance of Paramagnetic Organometallic Species in Activation, Selectivity and Catalysis*; Kluwer: Dordrecht, The Netherlands, 1989; pp 283–294.

(40) Ford, P. C.; Rudd, D. F. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.

(41) Kaim, W.; Kohlmann, S. *Chem. Phys. Lett.* **1987**, *139*, 365.

(42) Kohlmann, S. Ph.D. Thesis, University of Frankfurt, 1988.

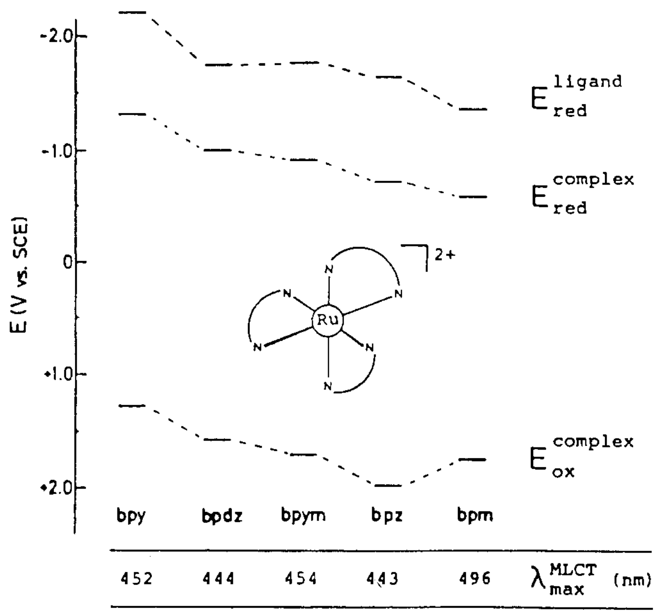


Figure 4. Ground-state redox potentials and MLCT absorption maxima of tris(bidiazine)ruthenium complexes in acetonitrile (reduction potentials of free ligands in DMF).

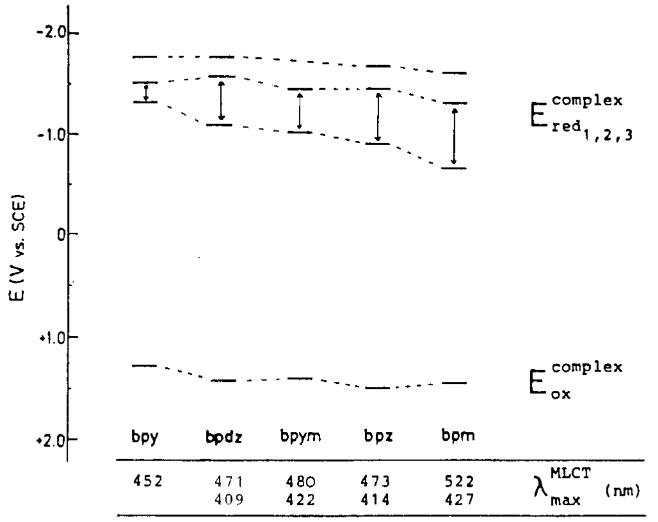


Figure 5. Ground-state redox potentials and MLCT absorption maxima of bis(2,2′-bipyridine)(bidiazine)ruthenium complexes in acetonitrile.

difference is found for the protons in 6′-positions, which are closest to the coordinating nitrogen centers.

We[30] and others[25e] have recently pointed out that symmetrically binuclear tris(chelate) complexes may exist as meso/DL diastereoisomers and presented corresponding NMR evidence for the complex $\{(bppz)[Ru(bpy)_2]_2\}^{4+}$.[30] The electrochemical and spectroscopic differences between these isomers must be very small, since no evidence for isomerism could be extracted from these methods.

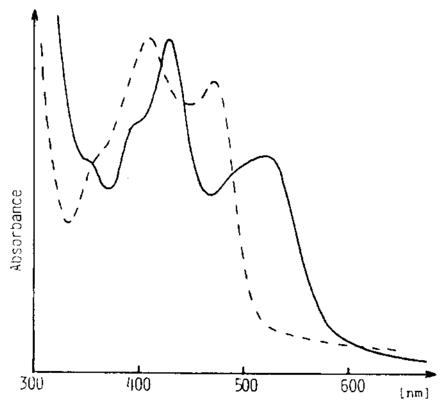


Figure 6. Absorption spectra of $[(bpm)Ru(bpy)_2]^{2+}$ (—) and of $[(bpdz)Ru(bpy)_2]^{2+}$ (---) in acetonitrile solution. The absorbance scale is different for each spectrum; for intensities cf. Table II.

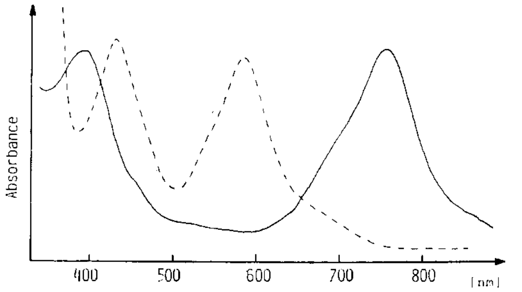


Figure 7. Absorption spectra of $[(bpy)_2Ru(abpy)Ru(bpy)_2]^{4+}$ (—) and of $[(bpy)_2Ru(bppz)Ru(bpy)_2]^{4+}$ (---) in acetonitrile solution. The absorbance scale is different for each spectrum; for intensities cf. Table II.

Redox Potentials from Cyclic Voltammetry. Tris(α-diimine)ruthenium(II) complexes can undergo several reversible redox processes which may involve metal oxidation ($Ru^{II} \rightarrow Ru^{III}$)[25,30] and ligand reduction ($L \rightarrow L^{\bullet-} \rightarrow L^{2-}$).[21,43] Interaction between identical, ligand-bridged metals on one hand and between identical, metal-bridged ligands on the other hand frequently causes a splitting of electrochemical waves;[30,43] ESR data for all singly reduced forms of the complexes shown in Chart III[8a,38a,45] will be reported separately.[44] Figure 3 shows some typical cyclic voltammograms; those of binuclear complexes were depicted in ref 30. Table I summarizes the electrochemical data for the complexes as obtained by us and others[13b,14a] in acetonitrile solution. Selected data for isomeric bidiazine complexes are displayed in Figures 4 and 5.

Electronic Spectra. Absorption of visible light by tris(α-diimine) complexes may lead to a relatively long-lived excited state of metal-to-ligand charge-transfer character as described by the simplified eq 2; this excited state may undergo electron transfer

$$[Ru^{II}(diimine)_3]^{2+} \xrightarrow[MLCT]{h\nu} {}^*[Ru^{III}(diimine^{\bullet-})(diimine)_2]^{2+} \quad (2)$$

in a bimolecular process, convert to an emissive state, dissociate, or undergo radiationless decay via a ligand field (d–d) excited state.[5,6] Absorption maxima of the complexes in Chart III in the visible region are summarized in Table II; for easier correlation with the electrochemical data according to eq 1 the energies are given in eV (1 eV = 8066 cm^{-1}). In agreement with the correlation obtained by Dodsworth and Lever for a series of ruthenium polypyridine complexes,[27] the difference χ comprising Franck–Condon contributions from intra- and intermolecular reorganization amounts to 0.18 ± 0.1 eV, an indication of relatively small structural changes on oxidation or reduction or in the MLCT excited state.

---

(43) (a) Ohsawa, Y.; Whangbo, M.-H.; Hanck, K. W.; Morris, D. E. *J. Am. Chem. Soc.* **1983**, *105*, 6522. (b) Ohsawa, Y.; Hanck, K. W.; DeArmond, M. K. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *175*, 229.

(44) Kaim, W.; Ernst, S. To be submitted for publication. Cf. also: Ernst, S. Ph.D. Thesis, University of Frankfurt, 1987.

(45) (a) Motten, A. G.; Hanck, K. W.; DeArmond, M. K. *Chem. Phys. Lett.* **1981**, *79*, 541. (b) Morris, D. E.; Hanck, K. W.; DeArmond, M. K. *J. Am. Chem. Soc.* **1983**, *105*, 3032. (c) Morris, D. E.; Hanck, K. W.; DeArmond, M. K. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *149*, 115. (d) Morris, D. E.; Hanck, K. W.; DeArmond, M. K. *Inorg. Chem.* **1985**, *24*, 977. (e) DeArmond, M. K.; Hanck, K. W.; Wertz, D. W. *Coord. Chem. Rev.* **1985**, *64*, 65. (f) Ohsawa, Y.; DeArmond, M. K.; Hanck, K. W.; Moreland, C. G. *J. Am. Chem. Soc.* **1985**, *107*, 5383. (g) Tait, C. T.; MacQueen, D. B.; Donohoe, R. J.; DeArmond, M. K.; Hanck, K. W.; Wertz, D. W. *J. Phys. Chem.* **1986**, *90*, 1766. (h) Gex, J. N.; DeArmond, M. K.; Hanck, K. W. *J. Phys. Chem.* **1987**, *91*, 251. (i) Berger, R. M.; McMillin, D. R. *Inorg. Chem.* **1988**, *27*, 4245.

Table I. Redox Potentials (V vs SCE) for Mono- and Binuclear Ruthenium(II) Complexes of α-Diimine Ligands[a]

complex	E_{ox}	E_{red_1}	E_{red_2}	E_{red_3}	E_{red_4}	ref
Ru(bpy)$_3^{2+}$	1.27	−1.31	−1.50	−1.77		13b
Ru(bpdz)$_3^{2+}$	1.58	−1.00	−1.25	−1.54		14b
Ru(bpm)$_3^{2+}$	1.75 (55)	−0.58 (55)	−0.73 (60)	−0.93 (83)		this work
Ru(bpz)$_3^{2+}$	1.98	−0.68	−0.87	−1.14		13b
Ru(bpym)$_3^{2+}$	1.69	−0.91	−1.08	−1.28		13b
Ru(abpy)$_3^{2+}$	>2.1	−0.02 (110)	−0.37 (90)	−0.87 (90)		this work
Ru(bpy)$_2$bpdz^{2+}	1.42 (60)	−1.06 (60)	−1.56 (60)	−1.77 (60)		
Ru(bpy)$_2$bpm^{2+}	1.45 (70)	−0.67 (70)	−1.30 (60)	−1.59 (55)	−1.74 (60)	this work
Ru(bpy)$_2$bpz^{2+}	1.49	−0.91	−1.45	−1.68		13b
Ru(bpy)$_2$bpym^{2+}	1.40	−1.02	−1.45			13b
Ru(bpy)$_2$abpy^{2+}	1.60 (100)	−0.36 (100)	−1.06 (100)			this work
complex	E_{ox_2}	E_{ox_1}	E_{red_1}	E_{red_2}	E_{red_3}[b]	ref
[Ru(bpy)$_2$]bpym^{4+}	1.69 (71)	1.53 (63)	−0.41 (68)	−1.08 (70)		15c
[Ru(bpy)$_2$]$_2$bppz^{4+}	1.58 (60)	1.39 (60)	−0.55 (60)	−1.09 (60)	−1.30 (100)	this work
[Ru(bpy)$_2$]$_2$bptz^{4+}	2.02 (70)	1.52 (60)	−0.03 (60)	−1.25 (i)	−1.55 (i)	this work
[Ru(bpy)$_2$]$_2$abpy^{4+}	2.22 (70)	1.67 (80)	+0.27 (60)	−0.39 (60)	−1.5 (90)	this work

[a] Data from cyclic voltammetry in CH$_3$CN/0.1 M tetraalkylammonium perchlorate. ΔE_p values (in mV) are given in parentheses; i denotes an irreversible process. [b] Multiple electron uptake by the bpy ligands.

Table II. Spectroscopic Data for Mono- and Binuclear Ruthenium(II) Complexes in Acetonitrile: Long-Wavelength Absorption Maxima λ (nm) or E_{op} (eV); Difference $\Delta E_{ox/red}$ between Reduction and Oxidation Potentials; Difference χ (eV) between E_{op} and $E_{ox/red}$; Emission Maxima E_{em} (eV); Difference $\Delta E_{abs/em}$ (eV) between Absorption and Pertinent Emission Energies; Calculated (Eq 3) Oxidation (E^*_{ox}) and Reduction Potentials (E^*_{red}) in the Lowest MLCT Excited State (V vs SCE)

complex	λ (log ε)	E_{op}	$\Delta E_{ox/red}$	χ	E_{em}	$\Delta E_{abs/em}$	E^*_{ox}	E^*_{red}	ref
Ru(bpy)$_3^{2+}$	451 (4.15)	2.74	2.61	0.13	2.00	0.74	−0.73	+0.69	13b
Ru(bpdz)$_3^{2+}$	444 (4.06) 410 (4.08)	2.79	2.58	0.21	1.95	0.84	−0.37	+0.95	14b
Ru(bpm)$_3^{2+}$	496 (3.81) 462 sh	2.50	2.33	0.17	1.77 1.89	0.73	−0.02	+1.19	this work, 46a
Ru(bpz)$_3^{2+}$	440 (4.11) 415 sh	2.80	2.66	0.14	2.03	0.77	−0.05	+1.35	13b
Ru(bpym)$_3^{2+}$	454 (3.93) 418 (3.91)	2.73	2.60	0.13	1.94	0.79	−0.25	+1.03	13b
Ru(abpy)$_3^{2+}$	517 (4.05) 478 sh	2.40	>2.12	<0.28	*a*		<0	>1	this work
Ru(bpy)$_2$bpdz^{2+}	471 (3.83) 409 (3.89)	2.63	2.48	0.15	1.77 1.87	0.86	−0.35	+0.71	this work, 46a
Ru(bpy)$_2$bpm^{2+}	526 (3.60) 506 sh 427 (3.75) 397 sh	2.37	2.12	0.25	1.67	0.70	−0.22	+1.00	this work, 46a
Ru(bpy)$_2$bpz^{2+}	473 (3.99) 414 (4.00)	2.62	2.40	0.33	1.75	0.87	−0.26	+0.84	13b
Ru(bpy)$_2$bpym^{2+}	480 sh 422 (398)	2.58	2.42	0.16	1.75	0.83	−0.35	+0.73	13b
Ru(bpy)$_2$abpy^{2+}	505 415	2.45	>1.96	<0.49	*a*				this work
[Ru(bpy)$_2$]$_2$bpym^{4+}	594 (3.91) 545 sh 411 (4.38)[b]	2.09	1.94	0.15	1.46[c] 1.61[c]	0.63 0.48	0.07	+1.05	12a, 15
[Ru(bpy)$_2$]$_2$bppz^{4+}	650 sh 584 (4.28) 548 sh 465 sh[b] 432 (4.30)	2.12	1.94	0.18	*a*				this work
[Ru(bpy)$_2$]$_2$bptz^{4+}	800 sh 685 (4.22) 575 sh 460 sh 404 (3.97)	1.80	1.55	0.25	*a*				this work
[Ru(bpy)$_2$]$_2$abpy^{4+}	850 sh 756 (4.36) 700 sh 453 sh 391 (4.35)	1.64	1.4	0.21	*d*				this work, 46b

[a] Not determined. [b] Transition d(Ru^{II}) → π^*_2(SLUMO). [c] Weak luminescence at 15 K. [d] No emission.

Emission maxima, if available, are also included in Table II as are the calculated (eq 3)[13b] redox potentials in the excited state.

$$E^*_{ox} = E_{ox} - E_{em} \qquad E^*_{red} = E_{red} + E_{em} \tag{3}$$

Differences ΔE between absorption and emission maxima are relatively constant with 0.87 ± 0.1 eV for the mononuclear systems. Binuclear systems were found to emit only very weakly (bpym complex)[12a] or not at all (abpy complex);[46b] in any case, the emission for the binuclear systems would be expected in the

---

[46] (a) Lever, A. B. P. Unpublished emission measurements. (b) Brauer, H. D. Near-infrared luminescence studies.

near-infrared region of the spectrum. Figure 6 shows absorption spectra of two new mononuclear $Ru(bpy)_2$ complexes while Figure 7 displays the spectra of two dimers.

Discussion

Tris(bidiazine) Complexes. Oxidation and first reduction potentials of the complexes are depicted in Figure 4 together with the reduction potentials of the free ligands. In agreement with Hückel MO calculated LUMO energies,[8] the reduction potentials of bdz ligands and of their ruthenium(II) complexes follow the ligand order bpy < bpdz ≈ bpym < bpz < bpm. However, the oxidation potentials show almost the same trend, viz., the ligand order bpy < bpdz < bpym ≈ bpm < bpz, which results from a corresponding sequence of ligand basicities (Chart V).[8] A correlation between pK_{BH^+}(ligand) and E_{ox}(complex) is shown in eq 4 (E_{ox} in V vs SCE) with the correlation coefficient $r = 0.987$, which allows us to estimate the unknown pK_{BH^+}(bpym) at about 2.2, a value similar to the value 2.65 obtained from the series of complexes $(bdz)Mo(CO)_2(PR_3)_2$.[8c]

$$pK_{BH^+}(\text{ligand}) = 11.73 - 5.64[E_{ox}(\text{Ru complex})] \quad (4)$$

According to the differences in redox potentials, which show a parallel behavior (Figure 4) for the bpy, bpdz, bpym, and bpz complexes, the long-wavelength MLCT band maxima display little variation with 448 ± 6 nm. Only the bpm complex stands out:[8] bpm is clearly the ligand with the lowest π^* level, but it is not the weakest base in that series (Chart V) so that facile reduction is not offset by a too-positive oxidation potential. Consequently, the MLCT absorption maxima for bpm complexes are shifted bathochromically by about 0.25 eV relative to those of the other isomers and of the bpy parent system.

The $[Ru(bpm)_3]^{2+}$ complex exhibits two clearly discernible absorption and emission bands, each showing a shoulder separated by about 0.15 eV; the complex $[Ru(abpy)_3]^{2+}$ displays two such absorption features separated by 0.19 eV. Since bpm has the largest LUMO/SLUMO (π_1^*/π_2^*) difference of all bidiazine ligands (including bpy)[8] and abpy an even larger such gap,[9b] these shoulders may be identified as symmetry-allowed MLCT transitions to the lowest π^* MO of the ligand from D_3-split (t_{2g}) metal levels;[47] an alternative interpretation would invoke vibrational splitting. Since the $(abpy)_3$ complex contains a very strongly π accepting but weakly basic α-iminoazo ligand,[24] the complex is reduced very easily whereas oxidation occurs only at very positive potentials. Nevertheless, the MLCT absorption maximum is bathochromically shifted still further than that of the bpm system or of the related *mer*-2-(phenylazo)pyridine complexes.[24]

Ruthenium tris(chelate) complexes containing three identical reducible ligands may serve as polyelectron-transfer agents.[43,48] It is therefore desirable to establish the ligand properties that govern the splitting of the three ligand-based reduction processes.[48] The series of the four isomeric bdz complexes and the abpy system exhibit remarkable variety in the splittings $E_{red}(2+/+/0/-)$, increasing in the ligand order bpm ≈ bpym < bpy ≈ bpz < bpdz ≪ abpy. Figure 3 illustrates the smallest total splitting of 0.35 V for the bpm complex and the largest overall difference of 0.85 V for the abpy system; again, the complexes with the least used,[49,50] deliberately selected ligands display the most extreme values. Two factors can be made responsible for this variability: Ligand–ligand interaction via the metal[7,31] depends, just like metal–metal interaction via a π conjugated ligand,[30,51] on the overlap between metal and ligand, i.e. on the electron density c_N^2 at the coordinating N centers in the LUMO (π_1^*) of the ligand.[30] Among the isomeric bidiazines, bpm and bpym have small such values (cf. Table III) whereas those of bpz and bpdz are large.[8] The abpy ligand exhibits particularly large values c_N^2(azo) values.[9]

Table III. Calculated Molecular Orbital Coefficients c_N^2 for α-Diimine Ligands L[8b] and Excited-State Lifetimes τ (μs) of Complexes RuL_3^{2+} at Room Temperature in Water[16]

L	c_N^2	τ	L	c_N^2	τ
bpy	0.139	0.61	bpz	0.170	0.75
bpdz	0.163	0.58	bpym	0.095	0.19
bpm	0.104	*a*			

[a] No luminescence detected in water;[16] however, see Table II.

The splitting of the reduction potentials for three initially identical chelate ligands is also determined by the amount of geometrical change after electron uptake, i.e. by the degree of freedom with which the ligands respond to electron transfer; the barrier toward electron "hopping" between the ligands after the first one-electron reduction is only about 0.1 eV in the $(bpy)_3$ and related complexes.[45] HMO–McLachlan calculations for the anion radicals[52,53] have shown a rather even spin distribution for the bpm system but a very strong perturbation response of the azo-containing bpdz isomer[52] so that the larger splitting for the $[Ru(bpdz)_3]^{2+/+/0/-}$ complex, especially in comparison to that for the bpm analogue, is not unexpected. The $[Ru(abpy)_3]^{n+/-}$ complex contains not only a ligand with a coordinating and potentially strongly "distorting"[5b] azo group[53] but also free 2-pyridyl substituents; significant geometric changes in orientation and π interaction within each ligand may contribute to the large redox potential difference and to not always ideally reversible electrochemical behavior.[24]

We have previously established the relevance of the calculated values c_N^2 for a variety of experimental results,[8,9,52,54] including the intensity of charge-transfer absorption bands.[8b] Although it is obvious that this value should affect all physical properties related to the charge transfer between metal and ligand, there have been no systematic attempts made to employ this knowledge for the design and selection of ligands.[26] Three important properties for the photochemical use of $[Ru(\alpha\text{-diimine})_3]^{2+}$ complexes shall be treated in the following.

(i) Studies on metal carbonyl complexes of the bidiazines have indicated a correlation between MLCT band intensity (or ϵ for bands of comparable shape and width) and c_N^2(LUMO, SLUMO) of the coordination centers.[8b] A similar pattern is observed for the ruthenium complexes where the bpm and bpym systems show small c_N^2(LUMO) and ϵ values while the bpz and bpdz isomers as well as the abpy and bpy systems have larger c_N^2(LUMO) values and more intense first MLCT bands (Tables II and III). From this argument, complexes[55] of ligands with very small such values in the lowest unoccupied MO such as certain tetraazaphenanthrenes[56] should exhibit very weak first MLCT transitions, which may be hidden within the long-wavelength envelope of more intense charge-transfer bands. In fact, Balzani, von Zelewsky, and co-workers have noted the failure of a correlation (eq 1) for one such system ("taphen") because reduction populates the LUMO (π_1^*) whereas the intense band observed corresponds to the MLCT process d (Ru) → SLUMO (π_2^*).[26i,55b]

(ii) An essential parameter for the applicability of a photosensitizer is the lifetime τ of the electron-transfer-active excited state.[5] While there have been attempts to assess this quantity in ruthenium and osmium bipyridyl complexes[26] by using for example the energy gap law[57] or vibrational data,[58,59] a comparison between reported data (at ambient temperature in aqueous solution)[14,16]

---

(47) Belser, P.; Daul, C.; von Zelewsky, A. *Chem. Phys. Lett.* **1981**, *79*, 596.
(48) Vlcek, A. A. *Coord. Chem. Rev.* **1982**, *43*, 39.
(49) For iron(II) complexes of bpm in aqueous solution cf. ref 32.
(50) Baldwin, D. A.; Lever, A. B. P.; Parish, R. A. *Inorg. Chem.* **1969**, *8*, 107.
(51) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.
(52) Kaim, W.; Ernst, S. *J. Phys. Chem.* **1986**, *90*, 5010.
(53) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3442.
(54) Alyea, E. C.; Malito, J.; Ernst, S. D.; Kaim, W.; Kohlmann, S. J. *Polyhedron*, in press.
(55) (a) Kirsch-deMesmaeker, A.; Nasielski-Hinkens, R.; Maetens, C.; Pauwels, D.; Nasielski, J. *Inorg. Chem.* **1984**, *23*, 377. (b) Juris, A.; Belser, P.; Barigelletti, F.; von Zelewsky, A.; Balzani, V. *Inorg. Chem.* **1986**, *25*, 256.
(56) Ernst, S.; Kaim, W.; Bessenbacher, C.; Vogler, C. Manuscript in preparation.
(57) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. Cf. also: Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.
(58) Balk, R. W.; Stufkens, D. J.; Crutchley, R. J.; Lever, A. B. P. *Inorg. Chim. Acta* **1982**, *64*, L49.
(59) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 106.

with the c_N^2(LUMO) values shows a conspicuous parallel (Table III).

Given the crude Hückel MO approximation used to determine c_N^2 values[8b,9b] and the uncertainty of lifetime measurements, one cannot expect a very good correlation between both parameters, yet the empirical trend (Table III) is that larger c_N^2(LUMO) values and therefore higher basicities of the reduced ligand in the MLCT excited state (eq 2) contribute to longer lifetimes, e.g. via a diminished probability for radiationless deactivation via thermally accessible ligand field (d–d) excited states. Points i and ii are connected via the underlying electron density parameter governing the extent of MO overlap and of charge transfer at the *metal/ligand "interface"*; an empirical correlation between ϵ and τ had been noted recently.[5b]

(iii) Photooxidation of substrates using $[\mathrm{Ru}(\alpha\text{-diimine})_3]^{2+}$ photosensitizers involves the formation of the radical cation as an intermediate reduction product.[5] Depending on the pH of the solution, these anion radical ligand[60] containing intermediates may be protonated, especially if additional coordination sites are available as in the bidiazine ligands. Pulse radiolysis studies have shown that the $[\mathrm{Ru(bpz)_3}]^+$ ion is a stronger base ($\mathrm{p}K_{\mathrm{BH^+}} = 7.1$) than the $[\mathrm{Ru(bpym)_3}]^+$ analogue with $\mathrm{p}K_{\mathrm{BH^+}} = 6.3$,[61] although the free ligand bpz is a weaker base than bpym (Chart V).[62] The reason for this initially puzzling reversal lies in the much higher electron densities c_N^2(LUMO) for the bpz ligand and in the larger orbital overlap with the positively charged metal center so that even the peripheral nitrogen centers ($c_N^2 = 0.096$ for bpz vs 0.056 for bpym)[8b] show significantly increased affinity toward $\mathrm{H^+}$,[61,62] $\mathrm{R^+}$,[63] and other electrophiles[64] after (partial) electron uptake.

Mononuclear Bis(2,2′-bipyridine)ruthenium Complexes. All non-bpy ligands employed in this study are more π electron accepting than this standard α-diimine molecule. The first electron added by the mixed complexes should thus be localized in the non-bpy ligand as has been demonstrated by ESR for the bpm[8a] and bpz[45h] system. The observed potentials behave accordingly (Figure 5), following the trend recognized for the tris(ligand) complexes. Further electrons may be accepted by the bpy ligands between −1.4 and −1.8 V vs SCE or once more by the non-bpy ligand, forming a dianionic chelate system.[43] It is not always easy to distinguish between both alternatives on the basis of established differences $E_{\mathrm{red_1}}/E_{\mathrm{red_2}}$ for the ligands;[8b,9b] in some instances, there may be "hopping"[45] of the second added electron between two different chelate ligands, for example between bpy and $\mathrm{bpm^{\bullet -}}$.

Ligand effects on the oxidation potentials of the $\mathrm{Ru(bpy)_2}$ complexes (Figure 5) are smaller than in the case of the tris(ligand) systems (Figure 4); nonetheless there is the same correlation between E_{ox}(complex) and $\mathrm{p}K_{\mathrm{BH^+}}$(ligand). However, the stronger increasing reduction potential now determines the energy of the absorption maximum, the bpm system exhibiting again the smallest transition energy. High flexibility of the "free" 2-pyridyl group in the abpy complex presumably causes the rather large difference χ (eq 1) between the transition energy at the band maximum and the redox range $\Delta E_{\mathrm{ox/red}}$. In general, the mixed-ligand complexes display two band systems in their absorption spectra, the feature at longer wavelengths being associated with a d (Ru) → π^* (non-bpy ligand) transition whereas the fairly constant band at about 415 nm is attributed to the d (Ru) → π^* (bpy) process.[13b] Both band systems can display short-wavelength shoulders (Figure 6).

Symmetrically Binuclear Bis(2,2′-bipyridine)ruthenium Complexes. Ligand-bridged binuclear systems show the additional effect of metal–metal interaction, illustrated by the splitting of the metal-based redox potentials, i.e. by the stability of the mixed-valence intermediate.[51] We have recently commented on the very different comproportionation constants for the four complexes described here, emphasizing the importance of the electron density at the coordinating centers in the lowest occupied MO.[30] In a localized description, strong back-donation by electron-rich ruthenium(II) to centers with high c_N^2(LUMO) causes an increase in ligand field strength at the *other* coordination centers,[40] thus lowering the reduction potential for the ruthenium(III) fragment and increasing the difference between both potentials.[30] The overall variation of E_{ox} (Table I) reflects the basicities of the bis-chelating ligands; apparently $\mathrm{p}K_{\mathrm{BH^+}}$ decreases along the series bppz > bpym > bptz > abpy. $\Delta E_{\mathrm{ox/red}}$ is particularly small for the abpy and bptz systems with their very low lying π^* (azo) orbitals, while the basic pyridyl chelate "arms" prevent the occupied metal d levels from becoming too stabilized.

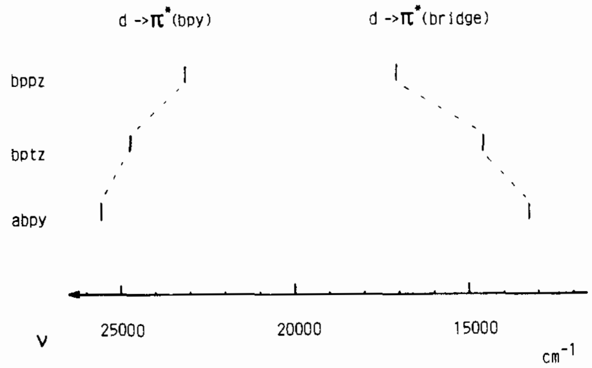


Figure 8. Divergence of MLCT I (d (Ru) → π^* (bridge)) and MLCT II (d (Ru) → π^* (bpy)) absorption maxima in binuclear complexes of $[\mathrm{Ru(bpy)_2}]^{2+}$.

Although E_{red}(bptz) > E_{red}(abpy),[9] the abpy complex is easier to reduce than the bptz system because coordination of the very polarizing dicationic $\mathrm{(bpy)_2Ru^{2+}}$ fragments constitutes a strong perturbation of the π system, thus lowering the LUMO of abpy with its large c_N^2 values[9b] relative to that of bptz. The singly reduced binuclear complexes show clear signs of localization, as demonstrated by a fairly well resolved ESR spectrum for the bptz derivative;[38a] the first two electrons are added to the bridging ligand with a potential difference typical for each ligand system.[9b] Reduction of the four bpy coligands occurs in two major waves at about −1.5 and −1.75 V vs SCE.

Not only does the lowering of the π^* level of the bridging ligand through *double* $[\mathrm{Ru(bpy)_2}]^{2+}$ coordination facilitate electron uptake but the result is also a significant bathochromic shift of the first MLCT band system in the visible spectrum. The binuclear bppz complex absorbs at distinctly lower energy than the isomeric system with the commercially available 2,3-bis(2-pyridyl)pyrazine analogue;[25b,d,26g,h] the reasons are the LUMO-lowering para substitution of the pyridyl groups in the bppz system and the inevitable nonplanarity of the π system in the 2,3-isomer.[25b,d,26h]

For the binuclear abpy and bptz complexes, an even larger bathochromic shift leads to complete separation of d (Ru) → π^* (μ-ligand) and d (Ru) → π^* (bpy) band systems (Figure 7) and allows the observation of shoulders (Table II). In all four binuclear complexes the two main MLCT bands are arranged symmetrically around a mean value of about 20 000 cm⁻¹ (500 nm, Figure 8); the significant hypsochromic shift of the d (Ru) → π^* (bpy) transition in complexes of the more π acidic ligands is a result of their lower ligand σ-donor strength in the ground state and thus a consequence of the mentioned dilemma (Figure 1); similar hypsochromic shifts of this transition have been observed for $\mathrm{Ru(bpy)_2}$ complexes of the weakly basic quinone ligands.[65,66]

---

(60) Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187.

(61) Venturi, M.; Mulazzani, Q. G.; Ciano, M.; Hoffman, M. Z. *Inorg. Chem.* **1986**, *25*, 4493.

(62) Crutchley, R. J.; Kress, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1983**, *105*, 1170.

(63) Kaim, W.; Matheis, W. Unpublished study.

(64) (a) Dodsworth, E. S.; Lever, A. B. P.; Eryavec, G.; Crutchley, R. J. *Inorg. Chem.* **1985**, *24*, 1906. (b) Toma, H. E.; Lever, A. B. P. *Inorg. Chem.* **1986**, *25*, 176. (c) Toma, H. E.; Auburn, P. R.; Dodsworth, E. S.; Golovin, M. N.; Lever, A. B. P. *Inorg. Chem.* **1987**, *26*, 4257.

(65) Haga, M.; Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1986**, *25*, 447.

(66) (a) Ernst, S.; Hänel, P.; Jordanov, J.; Kaim, W.; Kasack, V.; Roth, E. *J. Am. Chem. Soc.*, in press. (b) Kaim, W.; Kasack, V.; Binder, H.; Roth, E.; Jordanov, J. *Angew. Chem.* **1988**, *100*, 1229; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1174.

The first MLCT excited state of the binuclear systems can be formulated in a delocalized fashion as described by eq 5;[9b] only recently have such electronic structures been established for complexes in the ground state.[66,67]

$$[\mathrm{L}_n\mathrm{M}(\mu\text{-}\mathrm{L})\mathrm{ML}_n] \xrightarrow[\mathrm{MLCT}]{h\nu} {}^*[(\mathrm{L}_n\mathrm{M}^{\delta+})(\mathrm{L}^{\bullet-})({}^{\delta+}\mathrm{ML}_n)] \qquad (5)$$

The weak shoulders accompanying the main bands in the binuclear complexes may be due to vibrational structuring or to t_{2g} metal orbital splitting;[47] analysis of corresponding osmium analogues is currently in progress in order to make more definite assignments.[68] Further (weaker) transitions may result from MLCT transitions to higher unoccupied MOs of the bridging ligand; such bands have been clearly observed for the tetracarbonylmolybdenum complexes of bptz and bppz.[9b]

Owing to the 2-fold metal-to-ligand charge transfer in binuclear complexes, the corresponding bands are very intense. In agreement with calculated electron densities $c_N{}^2$(LUMO),[9b] the lowest intensity is found for the bpym complex whereas the binuclear abpy system exhibits the highest such value.

As in the series of the mononuclear tris(ligand) complexes, the abpy system exhibits the longest wavelength MLCT absorption reported for this class of compounds so far.[5] A preliminary search for luminescence of this material in the near-infrared region has not shown detectable emission,[46b] perhaps due to intramolecular quenching by the azo function.[69] In general, binuclear α-diimine complexes have been believed to be rapidly deactivated in the MLCT excited state,[12a,70] although emitting bi-, tri-, and tetranuclear species were reported recently.[25d,e,j] While no (Re^{I} [70]) or only weak emission (Ru^{II},[12a] Mo^{0} [71]) from MLCT excited states has been observed for binuclear bpym complexes, special conditions as found in a Cu^{I} dimer of bpym[72] and results for W^{0} and Re^{I} complexes of nonchelating pyrazine and related ligands demonstrate that there is a possibility for luminescence from binuclear systems.[73]

The use of weakly basic and strongly π accepting α-diimines and α-azoimines instead of bpy for long-wavelength-absorbing complexes results in a positive shift not only for the redox potentials in the ground state (Table I) but also for the calculated (eq 3)[13b] redox potentials of the first MLCT excited state (Table II). Lifetime permitting, these complexes should thus be useful primarily as photooxidizing sensitizers.[5,74]

Summary and Perspectives

By calculation-guided systematic ligand selection we have been able to obtain mono- and binuclear ruthenium(II) polyazine complexes that, in comparison to the many reported analogues,[5] exhibit rather extreme physical properties (E_{red}, E_{op}, K_c) within the respective class of complexes. Only small computational efforts are necessary to estimate relative π-orbital energies and the extremely valuable LUMO electron densities at the coordinating centers of the ligands;[8b,9b] their σ-donor strengths as represented by the basicities may be estimated or calculated as well.[18] Although the approach described here concerns only time-independent physical properties and cannot serve to assess the most critical reactivity of the excited states, the empirical connection between the $c_N{}^2$(LUMO) values and the lifetime of the MLCT excited state points to ways not only to rationalize experimental results for known compounds but also to guide the search for new α-diimine ligands and for photosensitizers derived thereof. The demonstrated success in correlating calculated with experimental properties has allowed an extensive screening of little or not yet used or not yet synthesized compounds as potential π-acceptor ligands in metal complexes;[44] results concerning e.g. the series of the two known[55] and the two unknown C_{2v} symmetric tetraazaphenanthrene chelate ligands will be reported in due course.[56] More than one century after the discovery of 2,2′-bipyridine and its colored complexes[2] ruthenium polyazine chemistry is thus about to enter an era in which the first question is not which ligands are *available* but which ones are *desirable*.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, Stiftung Volkswagenwerk, Flughafen Frankfurt/Main AG, and Fonds der Chemischen Industrie for financial support and Degussa AG, BASF AG, and Hoechst AG for generous donation of chemicals. A Karl Winnacker-Fellowship from Hoechst AG (W.K.) and Studienabschlussstipendium from the Fonds der Chemischen Industrie (S.D.E.) are gratefully acknowledged. We also thank Professors A. B. P. Lever (York University) and H. D. Brauer (Universität Frankfurt) for preliminary luminescence measurements.

---

(67) (a) Gross, R.; Kaim, W. *Angew. Chem.* **1987**, *99*, 257; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 251. (b) Kaim, W.; Gross, R. *Comments Inorg. Chem.* **1988**, *7*, 269.

(68) Kaim, W.; Kasack, V. Unpublished results.

(69) (a) Rau, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 224. (b) Albini, A.; Fasani, E. *J. Organomet. Chem.* **1984**, *273*, C26.

(70) Vogler, A.; Kisslinger, J. *Inorg. Chim. Acta* **1986**, *115*, 193.

(71) Kaim, W.; Kohlmann, S.; Lees, A. J.; Zulu, M. M. Manuscript in preparation.

(72) Hausen, H. D.; Kaim, W.; Kohlmann, S.; Kramer, H. E. A.; Rieker, J.; Vogler, C. Unpublished results.

(73) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711. Cf. also: Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 1139. Glezen, M. M.; Lees, A. J. *J. Am. Chem. Soc.* **1988**, *110*, 6243.

(74) Prasad, D. R.; Hoffman, M. Z. *J. Am. Chem. Soc.* **1986**, *108*, 2568.