then point to a LMCT or intraligand state as the excited state associated with reduction. However, our knowledge about the electronic structure of these complexes is insufficient for definitive conclusions. An interesting point is that the dominant, assigned electronic absorptions (Figure 1 and Table II) do not provide a rationale for the photochemistry of $[(CO)_5M=C=N=CR_2]^+$. The optically silent ligand field states are likely responsible for loss of CO, while a high-energy charge-transfer state leads to reduction products.

Whereas the W complex $[(CO)_5W=C=N=CMes_2]BF_4$ undergoes thermal as well as photochemical CO loss, the same is not true of $[(CO)_5Cr=C=N=CMes_2]BF_4$. Therefore, the photochemical conversion constitutes the only path to $BF_4\text{-}(CO)_4Cr(CNCMes_2)$. As evidenced by our synthesis of *trans*-$Br(CO)_4Cr(CNCMes_2)$, the complexes $BF_4(CO)_4M(CNCMes_2)$ are valuable starting materials for the synthesis of complexes of the type $X(CO)_4M(CNCMes_2)$. These have hitherto been completely unknown for M = Cr and were restricted to X = Cl, Br,

and I for M = W. Moreover, attempts to substitute Br^- in *trans*-$Br(CO)_4Cr(CNCMes_2)$ directly by X^- had proven unsuccessful. The reaction of $BF_4(CO)_4M(CNCMes_2)$ with X^- now makes a large number of complexes $X(CO)_4M(CNCMes_2)$ accessible.

Contribution from the Institut für Anorganische Chemie,
Niederurseler Hang, D-6000 Frankfurt am Main 50, West Germany

Four Bridging Bis Chelate Ligands with Very Low Lying π* Orbitals. MO Perturbation Calculations, Electrochemistry, and Spectroscopy of Mononuclear and Binuclear Group 6 Metal Tetracarbonyl Complexes

Wolfgang Kaim*[†] and Stephan Kohlmann

Received August 1, 1986

Coordination characteristics of the four bridging, π-delocalized bis chelate ligands 2,2′-bipyrimidine (bpym), 2,5-bis(2-pyridyl)pyrazine (bppz), 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz), and azo-2,2′-bipyridine (abpy) were evaluated with use of π molecular orbital perturbation calculations and were studied experimentally by example of mononuclear and binuclear complexes with the fragments $M(CO)_4$, M = Cr, Mo, W. The substantial stabilization of the π* (LUMO) levels in the order bpym, bppz, bptz, abpy strongly facilitates reduction of the complexes and causes shifts of the intense MLCT absorption bands out into the near-infrared region. Despite a notable activation barrier for the formation of binuclear abpy complexes with six-coordinate metals, the compound $(abpy)[Mo(CO)_4]_2$ was prepared and was shown to exhibit most remarkable spectral properties such as an intense yet rather narrow and little solvent sensitive MLCT absorption band at $11\,000$ cm^{-1}, with the next detectable absorption maximum lying above $30\,000$ cm^{-1}, a reduction potential close to that of the reference electrode, SCE, and closely spaced yet well-resolved CO stretching frequencies in the IR spectrum. All these spectral results can be correlated to π MO calculation data, which strongly suggest the use of bptz and abpy for studies concerned with ligand-mediated electronic interactions between metal centers. A particular asset of binuclear abpy complexes is the unusually short metal–metal distance caused by their coordination-induced "S-frame" conformation.

Introduction

Ligands that can serve as molecular bridges between metal centers and that also contain a delocalized π system have received considerable attention in recent years as potential electron "propagating" components (1) for inner-sphere electron-transfer reactions between metals,[1] (2) in magnetically coupled polynuclear systems ("superexchange"),[2] (3) in models for binuclear arrangements occurring in metalloenzymes,[3] and (4) in low-dimensional conducting coordination polymers.[4] Other conceivable applications of such bridged complexes include their use in multielectron storage systems for the activation of small molecules[2h] and as light-capturing antennas via charge-transfer (CT) transitions in the long-wavelength (near-infrared) region of the spectrum.[5a,6] Double coordination of metal fragments to such binucleating ligands is known to cause a particularly strong perturbation of the ligand π system, as is evident from pronounced spectroscopic effects.[5] Unfortunately, however, the dissociative stability of binuclear species is frequently diminished because of the reduced σ-donor strength of mononuclear complexes with

Chart I

bpym   bppz

bptz   abpy
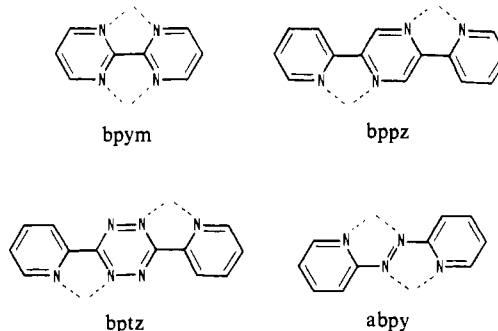
respect to a second coordination; this effect is typically illustrated by the coordination behavior of *doubly monodentate* bridging

---

(1) (a) Taube, H. *Electron Transfer Reactions of Complex Ions in Solution*; Academic: New York, 1970. (b) Haim, A. *Acc. Chem. Res.* **1975**, *8*, 264. (c) Gould, E. S. *Ibid.* **1985**, *18*, 22. (d) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980.

ligands such as pyrazine (pz)[2e,5c,d] or the 2,1,3-benzochalcogenadiazoles (bcd)[5b] (**1A**).

1A　　　　　**1B**

E = coordinating center
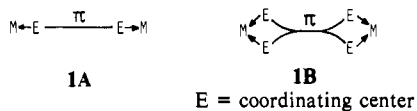
Improved binding conditions can be expected in complexes of *doubly bidentate* ligand bridges (**1B**), where the chelate effect contributes to dissociative stability. Within the important class of α-diimine ligands, the commercially available 2,2'-bipyrimidine (bpym) represents an example for such symmetrical systems and quite a number of homo- and heterobinuclear bpym complexes have been reported in recent years.[2g,3b,5e,f,h,7]

In a comparative study, we now present and discuss three related bis(α-diimine) and bis(α-azoimine) ligands, viz., 2,5-bis(2-pyridyl)pyrazine (bppz), 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz), and azo-2,2'-bipyridine (abpy), and their group 6 metal tetracarbonyl complexes (Chart I).

Coordination compounds of the last three ligands have been quite rare; some metal halide and pseudohalide complexes had been reported[8] before our preliminary communication.[5a] Our presentation of the coordination properties[9] of the four ligands

shown in Chart I includes a Hückel MO perturbation approach to metal coordination as well as correlations of these results with spectroscopic and electrochemical data; the strongly varying solvatochromism of binuclear tetracarbonylmolybdenum complexes[10a] and the ESR characteristics of binuclear complexes with bpym,[7e] bppz, and abpy anion radicals had been discussed previously.[10b]

Besides the electronic properties of the ligand, the metal–metal distances d_{M-M} are an important aspect in ligand-bridged bimetallic systems; obviously, the ligands bppz and bptz induce a similar distance d_{M-M} whereas bpym-[2g] and abpy-bridged[5a,10] binuclear complexes must have significantly shorter metal–metal distances. In comparison to other neutral binucleating ligands of this kind,[5g-k] the compounds shown in Chart I represent rather compact systems with 12 (bpym), 14 (abpy), and 18 (bppz, bptz) π centers; furthermore, the bptz and abpy ligands contain coordinating azo groups, which are known for their often unusual coordination chemistry.[11]

Experimental Section

Instrumentation: ^{1}H NMR, Bruker WH 270 and Varian A 60, solvent or Me4Si as internal standard; IR, Jasco A-100, solution spectra in THF; UV/vis/near-IR, Pye-Unicam SP 1800 and Perkin-Elmer Lambda 9; cyclic voltammetry, PAR system 363 with Bank VG 72 voltage scan generator, three-electrode configuration (glassy-carbon working electrode, saturated calomel reference electrode (SCE), Luggin capillary), 0.1 M solutions of tetrabutylammonium perchlorate in dry dimethylformamide (DMF) or acetonitrile, concentration of substrates during measurement about 10^{-3} M, 100 mV/s scan rate; elemental analyses, laboratory of Prof. W. Ried, Frankfurt, West Germany; Hückel MO calculations, available standard program[17] on a VAX 750/11 system.

All coordination compounds were synthesized and studied under an argon atmosphere with use of solvents dried by standard procedures. Chromatographic separation was carried out with increasingly polar solvents (hexane, toluene, tetrahydrofuran, acetone) on Florisil (Merck) columns.

Bppz,[12] bptz,[13] and abpy[14] were synthesized according to literature procedures (eq 3 and 4) and were checked for purity by NMR (cf. Table II); 2,2'-bipyrimidine was purchased from Alfa.

The binuclear complexes (μ-bpym)[Mo(CO)4]2,[7a] (μ-bppz)[Mo(CO)4]2,[10a] (μ-bptz)[Mo(CO)4]2,[5a] (μ-bptz)[W(CO)4]2,[5a] and (μ-abpy)[Mo(CO)4]2[5a] were prepared as reported (eq 3 and 4). Identity and purity of the products were established by spectroscopy and correct elemental analyses.

(μ-bppz)[Cr(CO)4]2. Reaction between bppz and 2 equiv of the photogenerated[15] complex (THF)Cr(CO)5 for 3 h in THF solution proceeds with CO evolution to give a dark blue solution. Precipitation with hexane and column chromatography (Florisil/THF) of the precipitate yield 20% of the compound. Anal. C, H, N.

(μ-bppz)[W(CO)4]2. Bppz and 2 equiv of the photogenerated[15] complex (THF)W(CO)5 are heated under reflux in THF solution for 1 h. Removal of the solvent and two recrystallizations from THF/hexane yield 75% of dark crystals. Anal. C, H, N.

(bptz)Cr(CO)4. Bptz and 1 equiv of (THF)Cr(CO)5 are allowed to react 3 h at ambient temperature. Precipitation with excess hexane and rapid recrystallization from THF/hexane yielded 20% of the sensitive

(2) (a) Sinn, E. *Coord. Chem. Rev.* **1970**, *5*, 313. (b) Inoue, M.; Kubo, M. *Ibid.* **1976**, *21*, 1. (c) Casellato, U.; Vigato, P. A.; Vidali, M. *Ibid.* **1977**, *23*, 31. (d) Hodgson, D. J. *Prog. Inorg. Chem.* **1974**, *19*, 173. (e) Kaim, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 171. (f) Kahn, O. *Ibid.* **1985**, *24*, 834. (g) Brewer, G.; Sinn, E. *Inorg. Chem.* **1985**, *24*, 4580. (h) Nishida, Y.; Shimo, H.; Maehara, H.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1985**, 1945. (i) Gatteschi, D.; Kahn, O.; Willett, R. D., Eds. *Magneto-Structural Correlations in Exchange Coupled Systems*; D. Reidel: Dordrecht, The Netherlands, 1984. (j) Hasty, E. F.; Colburn, T. J.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 2414. (k) Richardson, H. W.; Hatfield, W. E. *J. Am. Chem. Soc.* **1976**, *98*, 835.

(3) (a) Kurtz, D. M., Jr.; Shriver, D.; Klotz, I. M. *Coord. Chem. Rev.* **1977**, *24*, 145. (b) Petty, R. H.; Welch, B. R.; Wilson, L. J.; Bottomley, L. A.; Kadish, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 611. Cf. also: Brewer, G. A.; Sinn, E.; *Inorg. Chem.* **1984**, *23*, 2532. (c) Spiro, T. G., Ed. *Copper Proteins*; Wiley-Interscience: New York, 1981. (d) Morganstern-Badarau, I.; Cocco, D.; Desideri, A.; Rotilio, G.; Jordanov, J.; Dupre, N. *J. Am. Chem. Soc.* **1986**, *108*, 300. (e) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1986**, *25*, 398.

(4) (a) Hoffmann, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1983**, *16*, 15. (b) Hanack, M.; Seelig, F. F.; Strähle, J. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1979**, *34A*, 983. (c) Schneider, O.; Hanack, M. *Angew. Chem.* **1983**, *95*, 804; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 784. (d) Cf.: *Chem. Eng. News* **1985**, *63* (Sept 30), 22.

(5) (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. Chim. Acta* **1985**, *101*, L21. (c) Lees, A. J.; Fobare, J. M.; Mattimore, E. F. *Inorg. Chem.* **1984**, *23*, 2709. (d) Gross, R.; Kaim, W. *Ibid.* **1986**, *25*, 498. (e) Hunziker, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7370. (f) Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660. (g) Rillema, D. P.; Callahan, R. W.; Mack, K. B. *Ibid.* **1982**, *21*, 2589. (h) Rillema, D. P.; Mack, K. B. *Ibid.* **1982**, *21*, 3849. (i) Braunstein, C. H.; Baker, A. D.; Strekas, T. C.; Gafney, H. D. *Ibid.* **1984**, *23*, 857. (j) Gisselbrecht, J. P.; Gross, M.; Lehn, J. M.; Sauvage, J. P.; Ziessel, R.; Piccini-Leopardi, C.; Arrieta, J. M.; Germain, G.; van Meerssche, M. *Nouv. J. Chem.* **1984**, *8*, 659. (k) Haga, M. A.; Koizumi, K. *Inorg. Chim. Acta* **1985**, *104*, 47. (l) Brewer, K. J.; Murphy, W. R., Jr.; Spurlin, S. R.; Petersen, J. D. *Inorg. Chem.* **1986**, *25*, 882. (m) Kaim, W.; Ernst, S.; Kohlmann, S. *Polyhedron* **1986**, *5*, 445.

(6) Petersen, J. D.; Ruminski, R. R.; Eberle, E. C.; Behlow, H. W., Jr.; Brewer, K. J. *Coord. Chem.* **1984**, *23*, Mp8-4.

(7) (a) Overton, C.; Connor, J. A. *Polyhedron* **1982**, *1*, 53. (b) Watanabe, J.; Saji, T.; Aoyagui, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 327. (c) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1614. (d) Lanza, S. *Inorg. Chim. Acta* **1983**, *75*, 131. (e) Kaim, W. *Inorg. Chem.* **1984**, *23*, 3365. (f) Moore, K. J.; Petersen, J. D. *Polyhedron* **1983**, *2*, 279. (g) Ruminski, R. R.; Petersen, J. D. *Inorg. Chem.* **1982**, *21*, 3706.

(8) Bptz complexes: (a) Gustav, K.; Schmitt, C. J. *Z. Chem.* **1969**, *9*, 32. (b) Schilt, A. A.; Dunbar, W. E.; Gandrud, B. W.; Warren, S. E. *Talanta* **1970**, *17*, 649. Abpy complexes: (c) Baldwin, A.; Lever, A. B. P.; Parish, R. V. *Inorg. Chem.* **1969**, *8*, 107. (d) McWhinnie, W. R. *Coord. Chem. Rev.* **1970**, *5*, 293. (e) Beadle, P. J.; Grzeskowiak, R. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 245. (f) Beadle, P. J.; Grzeskowiak, R. *J. Chem. Soc. A* **1970**, 305. (g) Grzeskowiak, R.; Whatley, C.; Goldstein, M. *Spectrochim. Acta, Part A* **1975**, *31A* 1577. (h) Grzeskowiak, R.; Goldstein, M. *Inorg. Chim. Acta* **1979**, *33*, L153. (i) Rivarola, E.; Silvestri, A.; Alonzo, G.; Barbieri, R.; Herber, R. H. *Ibid.* **1985**, *99*, 87.

(9) (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.

(10) (a) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3306. (b) *Ibid.* **1986**, *25*, 3442. (c) Fenske, D.; Kaim, W.; Kohlmann, S., unpublished structural results. (d) Ernst, S.; Kurth, Y.; Kaim, W. *J. Organomet. Chem.* **1986**, *302*, 211.

(11) (a) Shunichiro, B.; Carter, D.; Fernando, Q. *Chem. Commun.* **1967**, *1301*. (b) Albini, A.; Kisch, H. *Top. Curr. Chem.* **1976**, *65*, 105 and literature cited therein. (c) Frazier, C. C., III; Kisch, H. *Inorg. Chem.* **1978**, *17*, 2736. (d) Fochi, G.; Floriani, C.; Bart, J. C. J.; Giunchi, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1515. (e) Albini, A.; Fasani, E. *J. Organomet. Chem.* **1984**, *273*, C26. (f) Fischer, G.; Sedelmeier, G.; Prinzbach, H.; Knoll, K.; Wilharm, P.; Huttner, G.; Jibril, I. *J. Organomet. Chem.* **1985**, *297*, 307. (g) Herberhold, M.; Leonhard, K. *Angew. Chem.* **1976**, *88*, 227; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 230.

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

(13) (a) Dallacker, F. *Monatsh. Chem.* **1960**, *91*, 294. (b) Geldard, J. F.; Lions, F. *J. Org. Chem.* **1965**, *30*, 318.

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

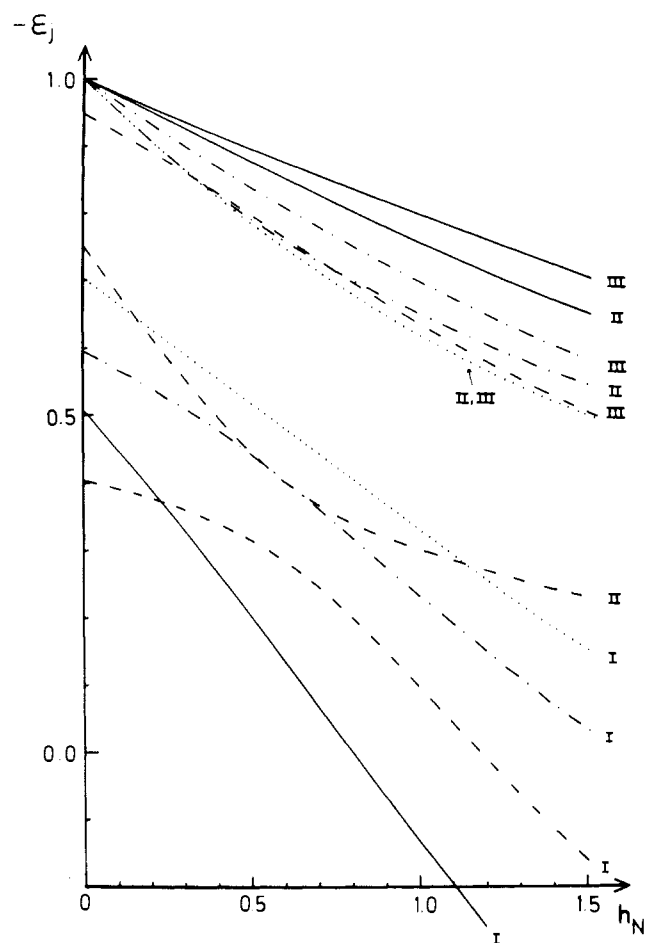(15) Strohmeier, W. *Angew. Chem.* **1964**, *76*, 873; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 730.

Figure 1. Correlation diagram of LUMO (I), SLUMO (II), and TLU-MO (III) energies from HMO perturbation calculations for binucleating bpym (···), bppz (−·−), bptz (---), and abpy (—) ligands vs. the Coulomb integral parameter h_N at the coordinating nitrogen centers (noncoordinating N center of bptz: $h_{N'} = 0.8$).

Table I. Squared π Molecular Orbital Coefficients c_N^2 at the Coordinating Nitrogen Centers for the Lowest Three Unoccupied π Levels of Binucleating Bis Chelate Ligands[a]

ligand		c_N^2 (LUMO)	c_N^2 (SLUMO)	c_N^2 (TLUMO)
bpym		0.095 (b_{2u})	0.080 (a_u, b_{3g})[b]	
		0.380 ($\sum^d$)	0.640 ($\sum$)	
bppz	N(pz)	0.146 (a_u)	0.108 (a_u')	0.014 (b_g)
	N(py)[c]	0.064	0.032	0.126
		0.420 ($\sum$)	0.280 ($\sum$)	0.280 ($\sum$)
bptz	N(azo)	0.250 (a_u')	0.034 (a_u)	0.037 (b_g)
	N(py)	0.000	0.079	0.118
		0.500 ($\sum$)	0.226 ($\sum$)	0.310 ($\sum$)
abpy	N(azo)	0.267 (b_g)	0.005 (a_u)	0.014 (b_g)
	N(py)	0.067	0.113	0.082
		0.668 ($\sum$)	0.236 ($\sum$)	0.192 ($\sum$)

[a] $h_N = h_{N'}$(bptz) = 0.8. [b] Degenerate levels. [c] N(py) = pyridine nitrogen center. [d] Sum $\sum c_N^2$ over all coordinating nitrogen centers.

complex, which had to be stored at temperatures below 0 °C; an elemental analysis could not be obtained due to marked decomposition at room temperature.

(bptz)Mo(CO)₄. Slow addition of 1 equiv of the complex (nbd)Mo-(CO)₄[16] (nbd = norbornadiene) in THF to a solution of bptz is necessary to preclude formation of the binuclear compound.[5a] After 1 h of stirring and removal of the solvent, recrystallization from THF/hexane yields 80% of the sensitive compound, which tends to form the binuclear species on standing as evident from elemental analysis and spectroscopy.

(abpy)Mo(CO)₄. The reaction of abpy with 1 equiv of (nbd)Mo-(CO)₄[16] in toluene solution proceeds within 30 min at room temperature. After removal of the solvent, column chromatography of the residue yields a blue zone (1/1 toluene/hexane), from which air-stable dark crystals are obtained after evaporation of most of the solvent and cooling to −28 °C; yield 39%. Anal. C, H, N. Formation of the more sensitive binuclear complex (μ-abpy)[Mo(CO)₄]₂ is not observed unless the reaction time is considerably longer (72 h); even then the yields of the binuclear compound remain low.[5a]

(abpy)Cr(CO)₄. The procedure given for the molybdenum analogue yields only 3% of the complex after column chromatography; the compound, like many such tetracarbonylchromium complexes,[9] decomposes fairly rapidly at room temperature (no elemental analysis).

¹H NMR, IR, electrochemical and UV/vis/near-IR data of the compounds are given later in Tables II–V and are discussed in the text.

Results and Discussion

1. π Molecular Orbital Perturbation Calculations. As conjugated polyaza π systems, the four ligands shown in Chart I are distinguished by having low-lying unoccupied (π^*) molecular orbitals (MOs). We have shown in a number of studies that the effect of metal or, more generally, electrophile coordination to

the nitrogen centers in such systems can be conveniently reproduced by employing a perturbation approach within the Hückel MO method for planar π systems,[17] viz., by varying the Coulomb integral parameter h_N of the potentially coordinating nitrogen centers.[18] A series of such calculations has been carried out now for the ligands shown in Chart I with the assumption of doubly bidentate coordination; the correlations of the energies of the lowest (LUMO), second lowest (SLUMO), and the third lowest unoccupied π MO (TLUMO) with the perturbation parameter h_N are shown in Figure 1.

The correlation diagram illustrates that the LUMO energies of the systems shown in Chart I are quite different indeed, following the sequence ϵ(bpym) < ϵ(bppz) < ϵ(bptz) < ϵ(abpy), except for small perturbation (h_N < 0.25) where ϵ(bptz) > ϵ(abpy). This crossing of orbital energies implies that the smaller abpy π system responds more strongly to the perturbation than the larger bptz ligand, a result for which experimental evidence will be presented later (part 6).
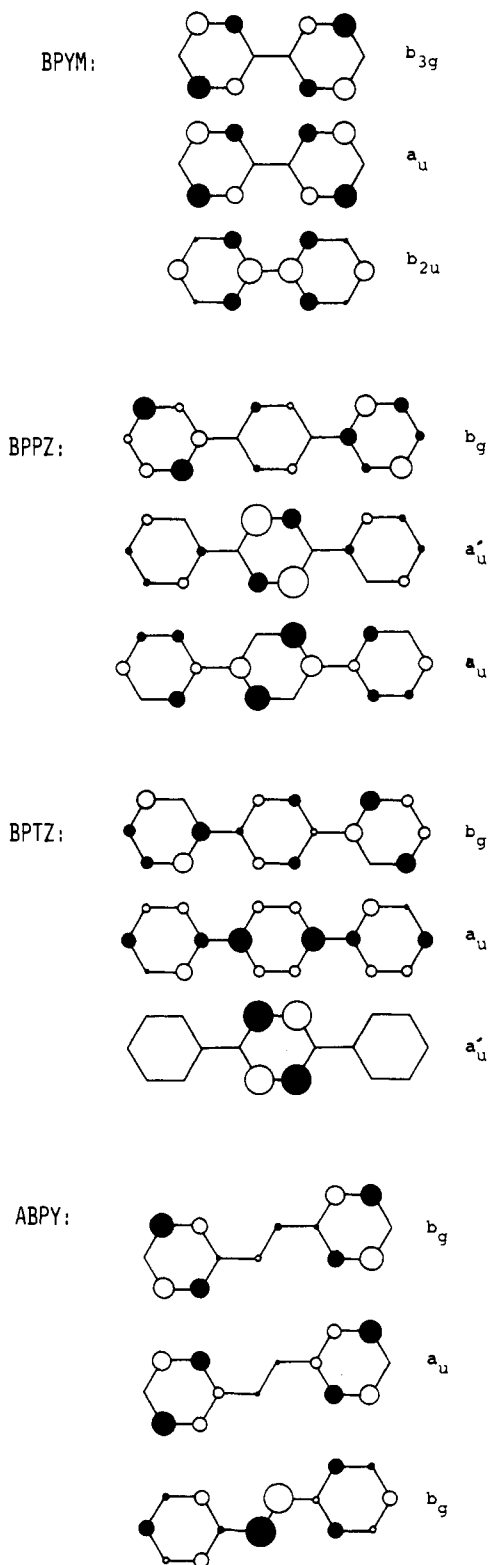
The energies of the higher unoccupied MOs of the systems shown in Chart I are quite close together with one notable exception, i.e. the rather low lying SLUMO of bptz. Within the manifold of the other SLUMO and TLUMO levels, the sequence of the LUMO energies is partly reversed; abpy in particular exhibits the highest lying SLUMO and TLUMO levels throughout the perturbation range. Accordingly, an unusually large gap exists between the lowest and the following unoccupied MOs in the abpy system whereas the other three ligands display a rather "normal" behavior[9] in this respect; many of the extraordinary spectroscopic properties of abpy complexes as described below can be attributed to this unique orbital level situation. Among other things, the accessibility of the ligand SLUMO in relation to the ligand LUMO may become important in the modifying of excited-state properties of corresponding charge-transfer complexes;[19] we had previously discussed similar, albeit less pronounced, variations in the series of the four isomeric mononucleating bidiazine systems.[9]

Further insight into the causes of these orbital energy differences is obtained from a study of the characters of the individual π MOs; Chart II shows the graphic representations of the MOs at a given

(16) Fischer, E. O.; Frölich, W. *Chem. Ber.* **1959**, *92*, 2995. Bennett, M. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 2037.

(17) Heilbronner, E.; Bock, H. *The HMO Model and its Application*; Wiley/Verlag Chemie: London/Weinheim, 1976; Vol. 1: (a) pp 156–239; (b) pp 396–410.

(18) (a) Kaim, W. *Chem. Ber.* **1981**, *114*, 3789. (b) Kaim, W. *J. Am. Chem. Soc.* **1982**, *104*, 3833, 7385. (c) Kaim, W. *J. Organomet. Chem.* **1983**, *241*, 157. (d) Kaim, W. *J. Am. Chem. Soc.* **1983**, *105*, 707. (e) Kaim, W. *J. Organomet. Chem.* **1984**, *264*, 317. (f) Kaim, W. *Inorg. Chem.* **1984**, *23*, 504, 3365. (g) Kaim, W. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 801. (h) Kaim, W.; Ernst, S. *J. Phys. Chem.* **1986**, *90*, 5010.

(19) (a) Balzani, V.; Carosetti, V. *The Photochemistry of Coordination Complexes*; Academic: New York, 1969. (b) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1. (c) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717. (d) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (e) Wacholtz, W. F.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* **1986**, *25*, 227.

Chart II. Graphic Representations of the Three Lowest Unoccupied π Molecular Orbitals (LUMO, SLUMO, TLUMO, in Ascending Order) of the Four Bis Chelate Ligands at $h_N = 0.8$

also an orbital reversal LUMO/SLUMO between the related 18-electron systems bppz and bptz. The value of these data for correlations with experimental results will become evident in later parts and had already been demonstrated in connection with ESR and ENDOR studies of the anion radicals and their complexes;[5m,7e,10b,53] the numbers of Table I explain that the abpy system responds most strongly to perturbation because it exhibits the largest sum of orbital coefficients $\sum c_N^2 = 0.688$ at the four coordinating centers whereas the least responsive system (bpym) exhibits the smallest, $\sum c_N^2 = 0.380$. Again, the reverse relation is found for the higher unoccupied MOs, where $\sum c_N^2$ is largest for bpym and smallest for the abpy system (Table I).

2. σ Coordination by the Ligands. Two features have to be considered in judging the suitability of an α-diimine ligand with regard to its electronic structure: the π-acceptor capacity and the σ-donor strength.[9,20,21b] Both components interact synergistically in the complexes via "back-bonding", so that a consideration of the ligand basicity (which refers to complexation with the simplest electrophile, H^+) is very useful.[9] Although dissociation constants of the ligands shown in Chart I have not yet been reported, some estimates can be made in view of related compounds: pK_{BH^+}, the pK_a of the conjugate acid of the base B, of 4,4'-bipyrimidine is 1.5,[9] and it might be assumed that the 2,2' isomer bpym has a similar value. 2-(Phenylazo)pyridine, a singly chelating ligand[21] related to abpy, was reported to have $pK_{BH^+} = 2.0$;[22] the value for the first protonation of abpy will probably be somewhat smaller. Furthermore, it can be assured that pK_{BH^+}(bppz) > pK_{BH^+}(bptz) because pyrazine is a stronger base than 1,2,4,5-tetrazine.[23]

In the absence of pK_{BH^+} values for the ligands shown in Chart I, their σ-donor capability must be extracted from other data such as oxidation potentials of coordinated metal fragments,[9,20,24] i.e. by measurement of the ligand field strength. Unfortunately, the group 6 metal tetracarbonyl complexes presented in this study do not exhibit reversible oxidation waves (part 6); the data from binuclear complexes with the $[Ru(bpy)_2]^{2+}$ fragment[5h,24a] suggest a decrease of σ-donor strength in the order bppz > bpym > bptz > abpy. At this point, it should be noted that the three C_{2h} ligands bppz, bptz, and abpy have been constructed such that they offer two different nitrogen coordination centers for each chelated metal atom: one less nucleophilic center, which is part of the π-electron-deficient pyrazine (bppz) or azo group (bptz, abpy), and one pyridyl center, which, by the good nucleophilic properties of pyridine,[23] compensates for the poor basicity of the other nitrogen atom and thus ensures sufficient dissociative stability. Although this separation of functions seems to be a rather simple approach for delocalized π systems, it was one of the major considerations in the choice of these particular ligand systems (Chart I), an important consequence of this arrangement being the loss of local C_{2v} symmetry (2).
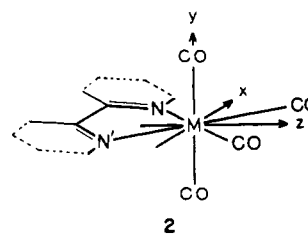

2

perturbation parameter while Table I summarizes the squared Hückel MO efficients c_N^2 at the coordinating centers of the doubly bidentate ligand systems shown in Chart I.

The data and the orbital representations illustrate the degeneracy of the SLUMO in the D_{2h} symmetry bpym system; the other ligands have only C_{2h} symmetry in their centrosymmetric conformations (Chart I). A further interesting aspect is that the nodal properties of 1,2,4,5-tetrazine allow only minute orbital coefficients at the pyridine ring centers in the LUMO of bptz;[5m,10b,53] note

(20) Crutchley, R. J.; Lever, A. B. P. *Inorg. Chem.* **1982**, *21*, 2276.
(21) (a) Krause, R. A.; Krause, K. *Inorg. Chem.* **1980**, *19*, 2600. (b) Krause, R. A.; Krause, K. *Ibid.* **1982**, *21*, 1714. (c) Krause, R. A.; Krause, K. *Ibid.* **1984**, *23*, 2195. (d) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Ibid.* **1981**, *20*, 2246; **1982**, *21*, 2737. (e) Datta, D.; Chakravorty, A. *Ibid.* **1983**, *22*, 1085. (f) Ghosh, B. K.; Mukhopadhyay, A.; Mukhopadhyay, A.; Goswami, S.; Ray, S.; Chakravorty, A. *Ibid.* **1984**, *23*, 4633.
(22) Foffani, A.; Foffani, M. R. *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1957**, *23*, 60; *Chem. Abstr.* **1958**, *53*, 824a.
(23) Cf.: Spanget-Larsen, J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 417 and literature cited therein.
(24) (a) Ernst, S.; Kaim, W., unpublished results. (b) Gross, R.; Kaim, W., unpublished results.

Table II. ^{1}H NMR Chemical Shifts (δ) of Ligands and Tetracarbonylmetal Complexes[a]

compd	$\delta_{H_{3,3'}}$	$\delta_{H_{4,4'}}$	$\delta_{H_{5,5'}}$	$\delta_{H_{6,6'}}$	$\delta_{H(pz)}$
bppz	8.45	7.86	7.37	8.74	9.66
(bppz)[Cr(CO)$_4$]$_2$	8.29	8.01	7.50	9.25	9.76
(bppz)[Mo(CO)$_4$]$_2$[b]	8.89	8.32	7.79	9.21	10.02
(bppz)[W(CO)$_4$]$_2$[b]	8.92	8.36	7.81	9.33	10.12
bptz	8.71	7.98	7.50	8.95	
(bptz)Mo(CO)$_4$	8.95	8.12	7.76	9.11	
	8.70	8.00	7.66	8.98	
(bptz)[Mo(CO)$_4$]$_2$	8.81	8.08	7.62	9.06	
abpy	8.0	8.0	7.48	8.76	
(abpy)Mo(CO)$_4$	8.0	7.92	7.42	8.70	
	8.50	8.0	7.52	9.21	
(abpy)[Mo(CO)$_4$]$_2$	9.17	7.98	7.53	9.04	

[a]From 60-MHz (ligands) and 270-MHz spectra (complexes) in CDCl$_3$ solution, except where indicated. Signals are split and assigned according to the typical coupling constants in pyridyl rings:[27] $J_{3,4}$ = 7.8–8.8 Hz; $J_{4,5}$ = 6.5–7.8 Hz; $J_{5,6}$ = 5.0–6.0 Hz; other J < 2 Hz. [b]In acetone-d_6.

A comparative discussion of electrochemical results and metal-to-ligand charge-transfer (MLCT) phenomena takes great advantage of a preceding consideration of the σ-donor properties of the reduced (anion radical) ligands;[9] an MLCT excitation involves, simply speaking, the generation of a complex of the ligand anion radical in the excited state (eq 1). Note that the MLCT

$$L_nM \longleftarrow (\mu\text{-}L) \longrightarrow ML_n$$

$$\downarrow \quad \begin{array}{l} \text{METAL-TO-LIGAND} \\ \text{CHARGE TRANSFER} \end{array} \qquad (1)$$

$$[L_nM^{\cdot} \longleftarrow (\mu\text{-}L^{\overline{\cdot}}) \longrightarrow M^{\cdot}L_n]^{*}$$
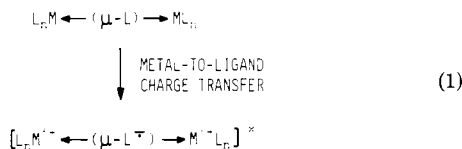
excited state of such symmetrical binuclear complexes can be formulated as a mixed-valence metal dimer bridged by an anion radical ligand (eq 1); the first ground-state complexes of this kind were obtained only recently.[24b]

Few pK_{BH^+} values of anion radical ligands are known; however, recent pulse radiolysis studies have demonstrated that the basicity of the α-diimine ligands bpy and 1,10-phenanthroline (phen) increases by about 20 orders of magnitude upon one-electron reduction.[25] We have recently employed the squared Hückel MO coefficients c_N^2 at the coordinating centers as an approximate measure for the relative σ basicity changes on going from the neutral to the reduced ligand according to eq 2,[9,17b] where μ is

$$\delta\Delta[E_\pi(\text{base}) - E_\pi(\text{acid})] = c_{N_\mu}^2(h_N - h_{N^+})\beta \qquad (2)$$

the level additionally occupied in the anion, h_N and h_{N^+} are the Coulomb integral parameters for base and acid, and β is the Hückel MO resonance integral; these data could be correlated with quite a variety of experimental results such as solvatochromism,[10a] absorptivities and shifts of MLCT absorption bands, lifetimes of MLCT excited states, and redox potential changes.[9] The significance of c_N^2 values had also been demonstrated in a study on the phen anion radical,[18b] for which simple MO methods predict a singly occupied MO (a_2) with very small coefficients c_N^2[26] whereas ESR experiments clearly show single occupation of the nearby b_1 orbital, which displays large coefficients at the coordinating nitrogen centers.[18b]

In application of eq 2 and the data of Table I, it is apparent that the weakest bases in the ground state (abpy, bptz) should receive the largest basicity increase on acquisition of negative

(25) Krishnan, C. V.; Creutz, C.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1983**, *105*, 5617.

(26) Ito, T.; Tanaka, N.; Hanazaki, I.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 702. Honeyburne, C. L. *Mol. Phys.* **1971**, *21*, 1057. Gooijer, C.; Velthorst, N. H.; MacLean, C. *Ibid.* **1972**, *24*, 1361. Held, R.; Dietz, F.; Thomas, P. *Z. Chem.* **1972**, *12*, 304. Gürtler, O.; Dietz, K. P.; Thomas, P. *Z. Anorg. Allg. Chem.* **1973**, *396*, 217. Rusina, A.; Vlcek, A. A.; Zalis, S. *Z. Chem.* **1979**, *19*, 27. Purcell, K. F. *Inorg. Chem.* **1984**, *23*, 4770.

charge in the π system whereas the stronger neutral state bases bpym and bppz should receive a smaller such increase in the reduced state.

3. Synthesis of Complexes. The group 6 metal tetracarbonyl complexes of the ligands shown in Chart I were obtained via two different routes, both of which involve rather mild reaction conditions: diolefin exchange with (nbd)M(CO)$_4$ complexes (eq 3 and 4) and THF and CO exchange of photogenerated (THF)M-

(3)

(4)
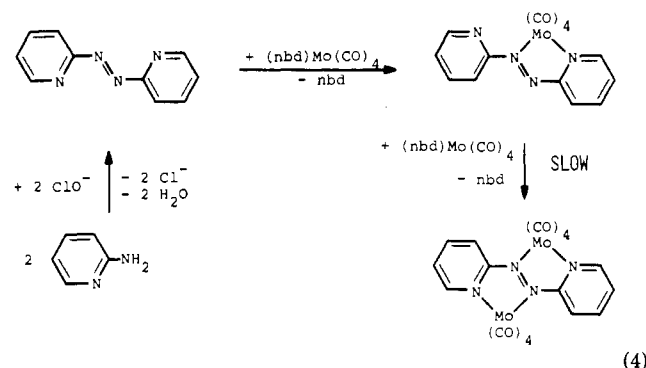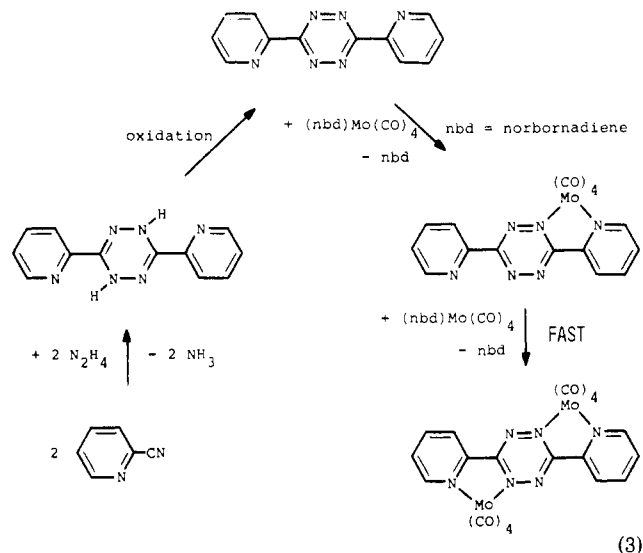
(CO)$_5$ complexes.[9] Whereas the binuclear bpym[7a,f] and bppz complexes are obtained without difficulty, we encountered synthetic problems with the other two, less nucleophilic ligands. Chromium tetracarbonyl complexes could be obtained by either method as mononuclear species; however, they proved to be thermolabile and showed decomposition at room temperature; similar observations were made for Cr(CO)$_4$ complexes of the less basic bidiazines.[9] The formation of tungsten complexes, on the other hand, requires thermal activation which has precluded e.g. the synthesis of the sensitive abpy complexes. Tetracarbonylmolybdenum complexes proved to be the most stable species, requiring only little activation for their formation (eq 3 and 4); however, we noted a conspicuous difference between bptz and abpy systems. With bptz, the formation of binuclear complexes proceeds very rapidly and special care is necessary to intercept only the mononuclear complex (eq 3). With the abpy ligand, on the other hand, the formation of the green binuclear complex (μ-abpy)-[Mo(CO)$_4$]$_2$ is very sluggish; several days of reaction time was necessary to obtain even small yields of the compound (eq 4), which tends to disintegrate at room temperature, especially in the presence of coordinating solvents. The reason for this conspicuously different behavior lies in the steric situation (3) as pointed out in parts 4 and 8.

4. ^{1}H NMR Spectra. The ^{1}H NMR data (Table II) of the ligands bppz, bptz, and abpy and of their binuclear complexes show the equivalence of the 2-pyridyl groups; the ligands probably have freely rotating pyridyl rings while the binuclear compounds must adopt a centrosymmetric C_{2h} conformation of the ligand

Table III. CO Vibrational Stretching Frequencies ν_{CO} (cm^{-1}) in THF Solution and Calculated[a,b] Force Constants k (mdyn/Å) of Tetracarbonylmetal Complexes

complex	$\nu_{CO}{}^b$				k_1	k_2	k_i
	A$_1$	B$_1$	A$_1$	B$_2$			
(bpym)Mo(CO)$_4$	2012 (m)	1905 (vs)	1890 (s)	1845 (s)	14.10	15.37	0.36
(bpym)[Mo(CO)$_4$]$_2$	2015 (m)	1920 (vs)	1895 (s)	1855 (s)	14.21	15.53	0.32
(bppz)[Cr(CO)$_4$]$_2$	1990 (m)	1900 (br, vs)		1830 (s)	13.83	15.18	0.30
(bppz)[Mo(CO)$_4$]$_2$	2002 (m)	1918 (vs)	1895 (s)	1850 (s)	14.10	15.42	0.29
(bppz)[W(CO)$_4$]$_2$	1990 (m)	1900 (br, vs)		1850 (s)	14.11	15.17	0.30
(bptz)Cr(CO)$_4$	2000 (m)	1895 (br, vs)		1850 (s)	14.16	15.18	0.34
(bptz)Mo(CO)$_4$	2005 (m)	1928 (br, vs)		1877 (s)	14.48	15.53	0.26
(bptz)[Mo(CO)$_4$]$_2$	1995 (vs)	1940 (br, s)		1875 (s)	14.39	15.58	0.19
(bptz)[W(CO)$_4$]$_2$	1979 (vs)	1935 (br, s)		1872 (s)	14.31	15.43	0.16
(abpy)Cr(CO)$_4$	2003 (m)	1945 (br, vs)		1891 (s)	14.64	15.67	0.20
(abpy)Mo(CO)$_4$	2008 (m)	1942 (br, vs)		1878 (s)	14.41	15.68	0.23
(abpy)[Mo(CO)$_4$]$_2{}^c$	1985 (s)	1945 (s)	1908 (s)	1872 (s)	14.29	15.56	0.15
	1985 (s)	1908 (s)	1945 (s)	1872 (s)	14.40	15.20	0.25

^{a} Cotton–Kraihanzel method.[29a] ^{b} Group symbols refer to local C_{2v} symmetry. ^{c} Upper assignment favored; cf. text.
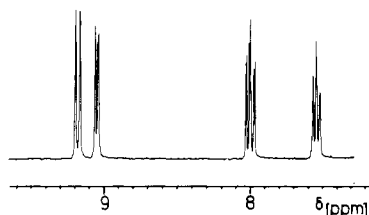

Figure 2. ^{1}H NMR spectrum of (μ-abpy)[Mo(CO)$_4$]$_2$ in CDCl$_3$ solution, showing unusual deshielding of protons H$_{3,3'}$ (doublet with larger coupling constant).

(Chart I). The mononuclear complexes studied display different proton resonances for each pyridyl ring. Assignments of the signals were made according to the established[27] coupling pattern and coupling constants for 2-substituted pyridyl systems. The typical sequence $\delta_{H_6} > \delta_{H_3} > \delta_{H_4} > \delta_{H_5}$ was found in all but one instance: The binuclear complex (μ-abpy)[Mo(CO)$_4$]$_2$ has $\delta_{H_{3,3'}} > \delta_{H_{6,6'}}$ (Figure 2).

To-scale drawings as shown in **3** and **4** suggest that the special deshielding of H$_{3,3'}$ must be the result of close contact between these protons and one of the equatorial carbonyl groups at the metal center coordinated to the other pyridine ring in the coordination-induced conformation (**3**) of the binuclear complex. This
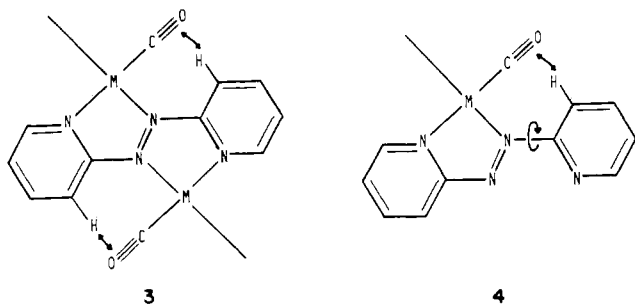

3   **4**

steric interaction must then also be responsible for the reluctance of the abpy ligand to form binuclear complexes (part 3, eq 4); such an interaction is absent in all other systems (Chart I). The normal sequence of δ_H(pyridyl) found for the mononuclear complex (abpy)Mo(CO)$_4$ suggests that the "free" pyridine ring does not adopt the unfavorable conformation **4** in solution, an assumption that is supported by X-ray crystallographic studies for the solid state.[28]

5. Carbonyl Vibrational Spectra. Four CO stretching bands are expected in the infrared spectra of *cis*-tetracarbonylmetal complexes; Table III shows that the two central bands overlap

Figure 3. IR spectrum of (μ-abpy)[Mo(CO)$_4$]$_2$ in the CO stretching region (THF solution).

in many cases. The bands have been assigned with use of the group notation for local C_{2v} symmetry (**2**), which can only be an approximation for the complexes with the last two ligands in the series shown in Chart I. Figure 3 shows the well-separated CO stretching bands of (μ-abpy)[Mo(CO)$_4$]$_2$; the intensity of the high-energy symmetry-forbidden "A$_1$" band found for binuclear abpy and bptz complexes is quite remarkable and seems to indicate considerable deviation from O_h symmetry. Additional perturbation of this symmetry should result from the nonbonded interactions (**3**) mentioned earlier and might be responsible for the separation of bands in the IR spectrum of the binuclear abpy complex (Figure 3).

Force constants have been calculated (Table III) according to the method of Cotton and Kraihanzel,[29a] and despite the limits of this approximation,[29,30] the calculated values reveal one important trend: The lowering of the ligand LUMO as one goes from bpym to abpy (Figure 1) correlates with a decrease of the interaction constant k_i; it was stated that k_i should increase with

(27) Cf.: Memory, J. D.; Wilson, N. K. *NMR of Aromatic Compounds*; Wiley: New York, 1982.

(28) Fenske, D.; Kohlmann, S.; Kaim, W., structural studies to be published.

(29) (a) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. (b) Kraihanzel, C. S.; Cotton, F. A. *Inorg. Chem.* **1963**, *2*, 533. (c) Cotton, F. A. *Ibid.* **1964**, *3*, 702.

(30) (a) Jernigan, R. T.; Brown, R. A.; Dobson, G. R. *J. Coord. Chem.* **1972**, *2*, 47. (b) Braterman, P. S. *Metal Carbonyl Spectra*; Academic: London, 1975. (c) Burdett, J. K.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *Inorg. Chem.* **1978**, *17*, 948.
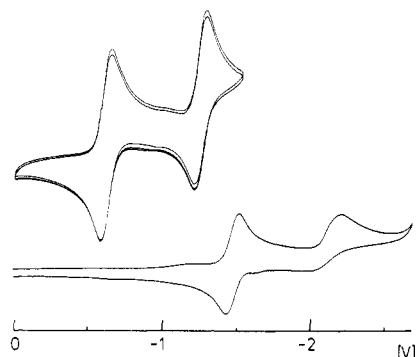
Figure 4. Cyclic voltammograms of bppz (bottom) and (μ-bppz)[Mo-(CO)$_4$]$_2$ (top) in DMF/0.1 M Bu$_4$N$^+$ClO$_4^-$ (SCE reference electrode, scan rate 100 mV/s).

increasing replacement of CO by ligands of lower π-bonding ability.[29a] Accordingly, the unusually small[29] k_i for (μ-abpy)-[Mo(CO)$_4$]$_2$ reflects particularly strong π bonding between this ligand and the zerovalent metal center; similarly small k_i values (illustrated by the small total range of 113 cm^{-1} for the four CO stretching bands) have only been observed with phosphorus halide ligands and related strong π acids.[29-31] The rather low absolute stretching frequencies and relatively small carbonyl stretching force constants (Table III), on the other hand, indicate rather weak σ bonding between the ligands shown in Chart I and the tetra-carbonylmetal fragments—in accordance with the dissociative lability observed in coordinating solvents. Nevertheless, the strong π interaction may compensate to some extent for the poor ligand nucleophilicity; the unusually[8c,21] low N≡N stretching frequencies of 1390 cm^{-1} (bptz complexes) and 1355 cm^{-1} (abpy complexes) illustrate this considerable π back-donation.

6. Redox Potentials. The ligands of Chart I and their Group 6 metal tetracarbonyl complexes were investigated by cyclic voltammetry in DMF solution. The dissociative lability of some of the binuclear complexes has made it necessary to perform some measurements also in acetonitrile solution; as was noted previously,[9] this change of solvent causes a negative shift of about 0.1 V for the reduction potentials. The electrochemical results are summarized in Table IV; oxidation potentials of the compounds could not be determined due to the strongly labilizing effect of these processes[32] on already labile systems, and anodic peak potentials were found between 0.6 and 1.0 V vs. SCE.[9,20,32]

In the case of reductive processes, the four ligands already exhibit reversible (ΔE = 60–80 mV) first and irreverisible second reduction waves in their cyclic voltammograms (Figure 4). Bptz is the most easily reduced ligand, followed by abpy, bppz, and bpym; this sequence is in agreement with the calculated LUMO energies for h_N < 0.25 (Figure 1). Coordination of tetra-carbonylmetal fragments shifts the reduction potentials to more positive values with binuclear complexes being more easily reduced than mononuclear species. The series of bppz complexes illustrate that compounds with the heavier homologues display more positive reduction potentials (Table IV); furthermore, the stabilization of reduced forms by coordination is also evident from the reversibility displayed by the equally shifted second reduction waves in some instances (Figure 4). The differences Δ = $E_{red}(-/2-) - E_{red}(0/-)$ are only slightly changed through metal fragment coordination and are thus characteristic for the ligand systems.[35a] The values $\Delta \approx$ 0.6–0.7 V for bpym and bppz[35a] and abpy[36] systems correspond to an anion radical stability constant $K \approx 10^{11}$ (eq 5); bptz,

$$K = [M^{\cdot-}]^2/[M][M^{2-}] = 10^{\Delta E/59 \; (mV)} \qquad (5)$$

(31) Stelzer, O.; Unger, E. *Chem. Ber.* **1975**, *108*, 1246.
(32) tom Dieck, H.; Kühl, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 324.
(33) Connor, J. A.; James, E. J.; Overton, C. *Polyedron* **1985**, *4*, 69.
(34) Tabner, B. J.; Yandle, J. R. *J. Chem. Soc. A* **1968**, 381.
(35) (a) Horner, M.; Hünig, S.; Pütter, H. *Electrochim. Acta* **1982**, *27*, 205. (b) Troll, T. *Ibid.* **1982**, *27*, 1311.
(36) Cf.: Cheng, S.; Hawley, M. D. *J. Org. Chem.* **1985**, *50*, 3388.

Table IV. Reduction Potentials E_{red} (V) of Ligands and Tetracarbonylmetal Complexes[a,b]

compd	$E_{red}(0/-)$	$E_{red}(-/2-)$
bpym[c]	-1.73	-2.44 (i)[b]
(bpym)Mo(CO)$_4$[c]	-1.07	-1.71 (i)
(bpym)[Mo(CO)$_4$]$_2$	-0.63	d
(bpym)[Mo(CO)$_4$]$_2$[e]	-0.67	-1.51
bppz	-1.49	-2.2 (i)
(bppz)[Cr(CO)$_4$]$_2$[f]	-0.74	-1.37
(bppz)[Mo(CO)$_4$]$_2$	-0.60	-1.23 (q)
(bppz)[W(CO)$_4$]$_2$[g]	-0.57	-1.18
bptz	-0.72	-2.2 (i)[d]
(bptz)Cr(CO)$_4$	-0.35	d
(bptz)Mo(CO)$_4$	-0.30 (q)[h]	d
(bptz)[Mo(CO)$_4$]$_2$	-0.07	d
(bptz)[Mo(CO)$_4$]$_2$[i]	-0.18	d
(bptz)[W(CO)$_4$]$_2$[j]	-0.06	d
abpy	-0.96	-1.60 (i)
(abpy)Cr(CO)$_4$	-0.55	d
(abpy)Mo(CO)$_4$	-0.55 (q)[h]	d
(abpy)[Mo(CO)$_4$]$_2$	+0.04[k]	d
(abpy)[Mo(CO)$_4$]$_2$[i]	-0.06	-0.73 (q)

[a] Data from cyclic voltammetry, potentials vs. SCE. The solvent is DMF, except where indicated; reduction potentials in acetonitrile are more negative by 0.1–0.2 V. [b] Legend: i, irreversible reduction processes with cathodic peak potentials given (scan rate 100 mV/s); q, quasi-reversible redox process. [c] Reference 9b. [d] Ill-defined wave(s). [e] In THF solution.[33] [f] Slow dissociation to mononuclear complex, E_{red}-(0/-) = -1.1 V. [g] Slow dissociation to mononuclear complex, $E_{red}(0/-)$ = -0.95 V. [h] Slow conversion to binuclear anion radical complex. [i] In acetonitrile solution. [j] Slow dissociation to mononuclear complex, $E_{red}(0/-)$ = -0.35 V. [k] Rapid dissociation in DMF solution.

on the other hand, exhibits a value Δ twice as large ($K > 10^{20}$). Such huge anion radical stability constants are characteristic for 1,2,4,5-tetrazine systems.[35b,37]

The calculated (Figure 1) perturbation behavior of the ligand π systems correlates with the response of the reduction potentials on metal coordination. The difference between the reduction potentials of ligand and binuclear Mo(CO)$_4$ complex is large for the bpym and abpy systems, which were also calculated to exhibit the steepest gradient $\delta(\epsilon_{LUMO})/\delta(h_N)$ (Figure 1). Bptz, on the other hand, shows a far less pronounced response toward this kind of perturbation, and accordingly, a crossing of LUMO levels was calculated between abpy and bptz. This crossing is nicely reflected by the fact that (abpy)[Mo(CO)$_4$]$_2$ is more easily reduced than (bptz)[Mo(CO)$_4$]$_2$ although the abpy ligand displays a reduction potential more negative than that of bptz (Table IV)! An approach of reduction potentials occurs also between the bpym and bppz systems, in full agreement with the calculations.

It was noted before that the coordination of a second metal fragment to a symmetrically binucleating ligand exerts a smaller contribution to the ligand-centered reduction[7e,10b] than the first coordination.[38] The abpy system, however, represents an exception to that rule (Table IV); this phenomenon is probably the result of a noncoplanar arrangement (4) of the mononuclear species because nonbonded interactions induce a twist of the free pyridyl ring, thereby preventing full delocalization of the 14 π electrons (Chart I). In the coordination-induced coplanar arrangement (3) full π delocalization becomes possible again, causing a large positive shift in the reduction potential of the complex to a value that is close to the reference potential of SCE. It is not surprising, therefore, that binuclear anion radical complexes of abpy and bptz are formed very easily through chemical reduction with electropositive metals or cobaltocene;[10b] their relative stability is also evident from the typical observation of binuclear anion radical complexes after reduction of mononuclear species (ECE mechanism).[38-40] ESR and ENDOR studies of the persistent and stable

(37) Kaim, W. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1633.
(38) (a) Kaim, W.; Kohlmann, S. *Inorg. Chim. Acta* **1985**, *101*, L21. (b) Gross, R.; Kaim, W. *Inorg. Chem.* **1986**, *25*, 498.
(39) Kaim, W. *J. Organomet. Chem.* **1984**, *264*, 317.

Table V. MLCT Absorption Maxima $\nu_{CT(1,2)}$ (cm^{-1}) of Tetracarbonylmetal Complexes in THF Solution^a

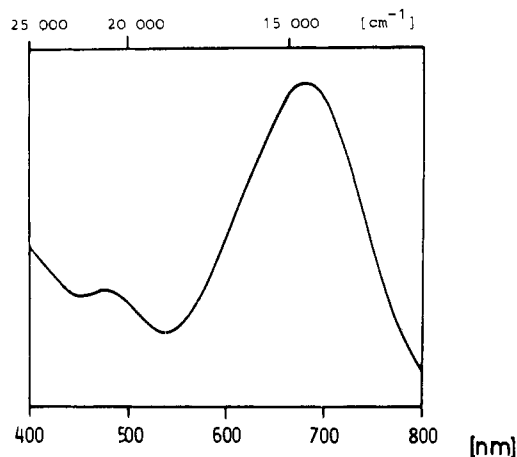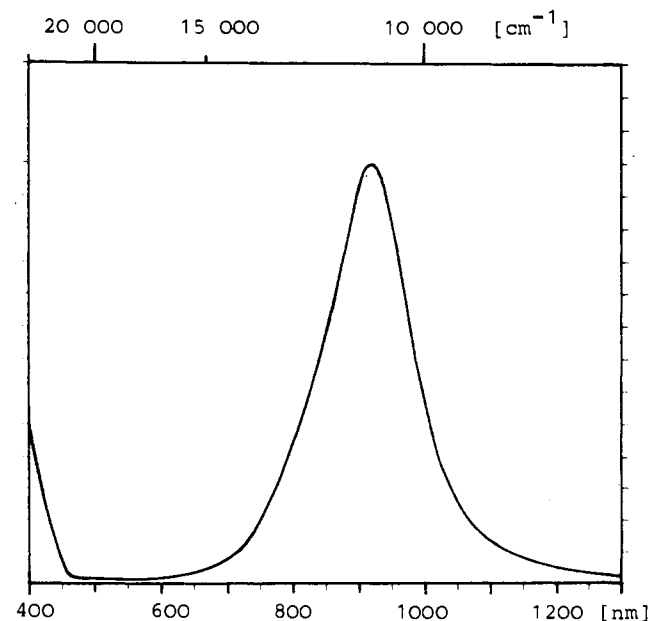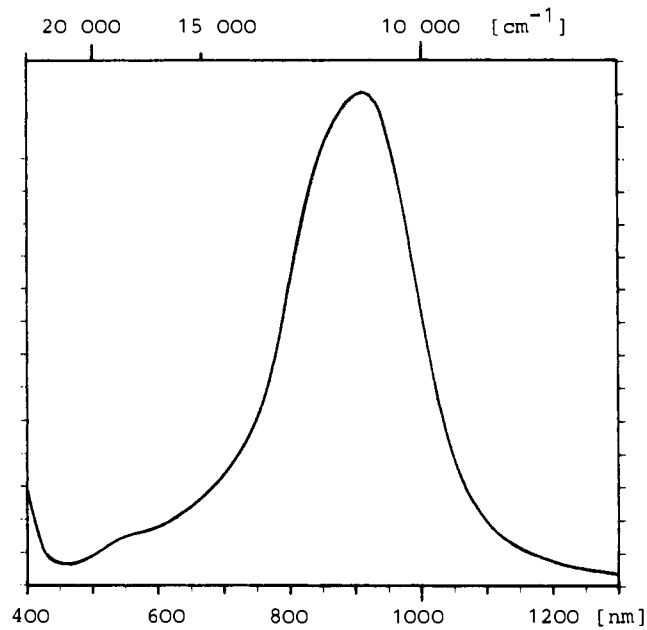| complex	$\nu_{CT(1)}$	$\nu_{CT(2)}$	$\Delta\nu_{CT}$
(bpym)Mo(CO)$_4$^{b}	20 400	26 500^c	6 100
(bpym)[Mo(CO)$_4$]$_2$	16 500 (5000^d)	23 500^c	7 000
(bppz)[Cr(CO)$_4$]$_2$	14 140	20 200	6 060
(bppz)[Mo(CO)$_4$]$_2$	15 200 (3000^d)	21 650	6 450
(bppz)[W(CO)$_4$]$_2$	14 750	20 830	6 080
(bptz)Cr(CO)$_4$	14 900	e	
(bptz)Mo(CO)$_4$	16 050	25 000	8 950
(bptz)[Mo(CO)$_4$]$_2$	11 780 (2800^d)	18 500^{f,g}	6 720
(bptz)[W(CO)$_4$]$_2$	11 700	18 500^f	6 800
(abpy)Cr(CO)$_4$	15 900	e	
(abpy)Mo(CO)$_4$	16 130	$\geq$33 000	$\geq$16 870
(abpy)[Mo(CO)$_4$]$_2$	11 100 (2100^d)	$\geq$32 000	$\geq$20 900

^{a} Values in other solvents and extinction coefficients of binuclear molybdenum complexes in ref 10a. ^{b} Reference 10d. ^{c} Partly obscured by transition at 26 000 cm^{-1}. ^{d} Half-width (cm^{-1}) of band. ^{e} Not determined. ^{f} Low-intensity band, log $\epsilon \leq 3.0$. ^{g} Next absorption maximum at 30 000 cm^{-1}.

($K > 10^{10}$) M(CO)$_4$ complexes of bpym[7e] as well as of bptz and abpy anion radicals have been reported separately,[10b,41] showing clear evidence for ligand-centered reduction.

7. MLCT Absorption Spectra. There has been a strong interest in complexes with low-energy metal-to-ligand charge-transfer (MLCT) transitions in recent years because many of these complexes are photostable in solution and have long-lived MLCT excited states from which luminescence[42,43] and electron-transfer reactions[44] can take place. Table V shows the energies of the first and second absorption band maxima for the tetracarbonylmetal complexes of the ligands shown in Chart I in THF; the remarkably different solvatochromic behavior of the centrosymmetric binuclear Mo(CO)$_4$ complexes was discussed elsewhere.[10a]

Starting with the first long-wavelength MLCT absorption band, previous studies on other α-diimine tetracarbonylmetal complexes have shown that this band can comprise several transitions from filled d levels to the unoccupied lowest π^* orbital of the ligand, the dominating, symmetry-allowed component being a $\pi^*_1 \leftarrow d_{yz}$ (2) transition.[45] The comparison of tetracarbonylmetal complexes in Table V shows that the sequence calculated for ligand LUMOs (π^*_1) and measured for the reduction potentials is also found for the MLCT absorption energies. The binuclear complex (μ-abpy)[Mo(CO)$_4$]$_2$ has the smallest transition energy with an absorption maximum in the near-infrared region of the spectrum;[5a] an unusually low charge-transfer transition had already been reported for a ferrous complex of abpy.[8c,d] Binuclear (bptz)[M-(CO)$_4$]$_2$ compounds exhibit only slightly larger transition energies

Figure 5. Electronic absorption spectrum of (μ-bppz)[Cr(CO)$_4$]$_2$ in the visible region (acetone solution).

Figure 6. Electronic absorption spectra of (μ-bptz)[Mo(CO)$_4$]$_2$ (top) and (μ-abpy)[Mo(CO)$_4$]$_2$ (bottom) in the vis/near-IR region (toluene solutions).

(40) Gross, R.; Kaim, W. *Angew. Chem.* **1985**, *97*, 869; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 856.

(41) Ligand-centered reduction of (μ-bppz)[M(CO)$_4$]$_2$ complexes: Kaim, W.; Kohlmann, S., unpublished ESR results.

(42) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979.

(43) (a) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (b) Giordano, P. J.; Fredericks, S. M; Wrighton, M. S.; Morse, D. L. *Ibid.* **1978**, *100*, 2257. (c) Giordano, P. J.; Wrighton, M. S. *Ibid.* **1979**, *101*, 2888. (d) Lees, A. J. *Ibid.* **1982**, *104*, 2038. (e) Lees, A. J.; Adamson, A. W. *Ibid.* **1982**, *104*, 3804. (f) Chun, S.; Lees, A. J. *Inorg. Chim. Acta* **1982**, *65*, L167. (g) Chun, S.; Palmer, D. C.; Mattimore, E. F.; Lees, A. J. *Ibid.* **1983**, *77*, L119. (h) Lees, A. J.; Fobare, J. M.; Mattimore, D. F. *Inorg. Chem.* **1984**, *23*, 2709. (i) Manuta, D. M.; Lees, A. J. *Ibid.* **1983**, *22*, 572. (j) van Dijk, H. K.; Servaas, P. C.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1985**, *104*, 179. (k) Servaas, P. C.; van Dijk, H. K; Snoeck, T. L.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1985**, *24*, 4494.

(44) (a) Wrighton, M. S.; Markham, J. *J. Phys. Chem.* **1973**, *77*, 3042. (b) Demas, N.; Diemente, D.; Harris, E. W. *J. Am. Chem. Soc.* **1973**, *95*, 6864. (c) Demas, N.; Harris, E. W.; McBride, P. P. *Ibid.* **1977**, *99*, 3547. (d) Luong, J. C.; Nadjo, L.; Wrighton, M. S. *Ibid.* **1978**, *100*, 5790.

(45) (a) Staal, L. H.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1978**, *26*, 255. (b) Balk, R. W.; Stufkens, D. J.; Oskam, A. *Ibid.* **1978**, *28*, 133. (c) Balk, R. W.; Stufkens, D. J.; Oskam, A. **1979**, *34*, 267.

while corresponding bppz and bpym complexes absorb in the visible region (Table V). Mononuclear complexes also exhibit a pattern that closely correlates to the measured reduction potentials, including the special behavior of the mononuclear abpy systems because of their probable noncoplanarity (**4**). It is evident from the close correspondence between calculated results (Figure 1), measured reduction potentials (Table IV), and the MLCT absorption energies that the LUMO largely determines the energy of the MLCT transition; this one-electron picture thus suggests that the metal levels are much less affected by the change within the ligands shown in Chart I. In agreement with previous observations,[9] the chromium complexes display the lowest and the molybdenum species the highest MLCT transition energies because the metal-centered HOMO is most destabilized in $Cr(CO)_4$ compounds.[32]

Table V and Figures 5 and 6 illustrate that the bpym,[7a,f,10a] bppz, and bptz complexes exhibit at least one discernible second MLCT band in the visible region of the spectrum. The assignment of these less intense features as second MLCT absorptions is supported by their solvatochromism[10a] and is fully compatible with the MO calculations (Figure 1), which revealed SLUMOs rather close in energy to the LUMOs of these three ligands.

A very different situation is encountered with the abpy complexes: In agreement with the very large SLUMO/LUMO gap (Figure 1), we could not detect any additional major absorption maximum, e.g. in the spectrum of $(abpy)[Mo(CO)_4]_2$ (Figure 6), until the UV region, where intraligand ($\pi^* \leftarrow \pi$) and other transitions dominate the electronic spectrum. For this binuclear $Mo(CO)_4$ complex, a most unusual situation results: The compound shows intense ($\epsilon > 10^4$)[10a] absorptions both in the UV and in the near-infrared (near-IR) regions of the spectrum but exhibits a wide absorption gap ($\Delta\delta_{max} > 20\,000$ cm^{-1}!) throughout the visible region;[5a] solutions of the complex have a faint green color because of the tails from both band systems in the visible region (Figure 6).

In assigning MLCT absorption bands with the help of π MO calculations of the ligands, we note that the band intensities correlate with the sum $\sum c_N^2$ of the squared HMO coefficients at the coordinating nitrogen centers.[9] This result is due to the fact that the transition probability depends on the square of the integral (shown by I) so that, to a first approximation, the π^* MO wave function is largely responsible for the relative band intensities; the π^* levels of different symmetries (Chart II) can interact in a symmetry-allowed fashion with one of the three high-lying filled d orbitals.[45]

$$\int_V \psi_n \mathbf{r} \psi_m \, dV \qquad \text{(I)}$$

Although a quantitative correlation of $\sum c_N^2$ vs. ϵ_{MLCT} cannot be expected for the present series of nonisomeric ligands (Chart I), the data from Table I and Chart II allow us to explain several experimental results. This includes the large absorptivities of abpy and bptz complexes ($\epsilon = 20\,000$–$30\,000$) in comparison with those of their bppz and bpym analogues ($\epsilon = 5000$–$20\,000$, first MLCT band);[10a] the intensity of the second MLCT band, on the other hand, decreases markedly on going from bpym[7f,10a] via bppz (Figure 5) to bptz complexes (Figure 6)—in full agreement with the $\sum c_N^2$(SLUMO) values (Table I). Not only does the LUMO degeneracy of the bpym system cause a high intensity of the second MLCT band but it is also responsible for the particularly strong solvatochromism of this spectral feature.[10a] The spectra of binuclear bpym complexes (D_{2h} symmetry) are further distinguished by a strong ($\epsilon \approx 12\,000$) solvent-insensitive band at 26 000 cm^{-1}.[7a,f,10a] This band was assigned as a ligand field (d* $\leftarrow$ d) transition with substantial MLCT character,[7f] yet the absence of such a dominant feature in the spectra of the C_{2h} symmetric binuclear complexes of bppz, bptz, and abpy requires a more detailed consideration (cf. below). The presence of an unusually low lying MO in binuclear bpym complexes is also evident from ESR studies on the anion radical species,[7e,46] which, in contrast

to the case for all other such complexes, have a $\langle g \rangle$ value smaller than $g_{electron} = 2.0023$.[5m,7e,10b,18f–h]

Another conspicuous spectral property must be noted when discussing band intensities: the half-width of the first MLCT absorption band decreases markedly in the series bpym $\rightarrow$ abpy (Table V); compared to typical band half-widths of 3000–4000 cm^{-1} for MLCT absorptions of α-diimine tetracarbonylmetal complexes,[9,45,47] the bands of binuclear bpym complexes are rather broad and those of abpy complexes relatively narrow. Although there is a multitude of factors that can influence the width of an absorption band,[48] charge-transfer bands owe most of their broadness to the large geometrical change in the relaxed MLCT excited state where metal and ligand have different formal oxidation states (eq 1). Apparently, this geometrical change is rather small for complexes of abpy but rather large for binuclear bpym compounds; such a conclusion had been obtained independently from an explanation of extraordinary solvatochromic behavior of these complexes. If we carry out this hypothesis further, this assumption also suggests that emission from MLCT excited states may be most unfavorable for binuclear bpym systems; in fact, no emission was observed from $\{(\mu\text{-bpym})[Ru(bpy)_2]_2\}^{4+}$ in fluid solution.[5e,l,7c]

8. Structural Aspects. An important property of binucleating ligands is their ability to keep two metals fixed at a well-defined distance. The metal–metal distance d_{M-M} in a ligand-bridged binuclear complex depends, of course, on the distance between the metals and the coordinating atoms; however, the contribution from the ligand size and conformation is more essential. From the model of Richardson and Taube[49] with a standard metal–nitrogen distance of 200 pm, the calculated values d_{M-M} are 690 pm (bppz, bptz), 520 pm (bpym), and 460 pm (abpy). The last value is significantly shorter than the distance d_{M-M} calculated for N_2-bridged complexes,[49] a result of the formal twisting in such "S-frame" ligands[28] as depicted in **5**.

5
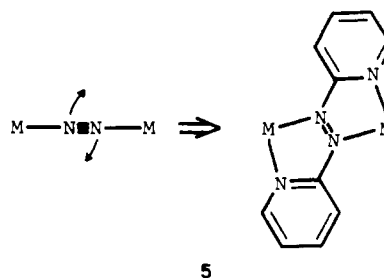
Medium-range metal–metal distances are of interest for "inorganic" electron-transfer studies[1,50] and for investigations on magnetic exchange interactions;[2,3] in agreement with the figures given above, recent experimental studies gave $d_{Co-Co} = 575$ pm in $(\mu\text{-bpym})[Co(hfa)_2]_2$, with $d_{N-Co} = 215$ pm (hfa = hexafluoroacetylacetonate),[2g] and $d_{Cu-Cu} = 494$ pm in $\{(\mu\text{-abpy})[Cu(PPh_3)_2]_2\}^{2+}$, which has $d_{N-Cu} = 210$ pm.[28] Although the formation of binuclear abpy complexes with six-coordinate metals requires some activation because nonbonded interactions impede the reaction **4** $\rightarrow$ **3**, there are compounds such as $\{(\mu\text{-abpy})[Ru(bpy)_2]_2\}^{4+}$ available[5a] that should allow a detailed study of medium-range metal–metal interactions.

It may be noted at this point that binuclear bpym complexes of transition metals have the metal d_{yz} orbitals (**6**) pointing toward each other, thereby creating the opportunity for direct metal–metal overlap, which may be responsible for the strong absorption band at 26 000 cm^{-1}. In the other binuclear systems (Chart I), the metal d orbitals are arranged in a staggered fashion so that their direct interaction is disfavored despite the possibility of short metal–metal distances (**6**, abpy). The use of bpym *and* one of the other ligands

(46) Kaim, W. *Coord. Chem. Rev.*, in press.

(47) tom Dieck, H.; Franz, K. D.; Hohmann, F. *Chem. Ber.* **1975**, *108*, 163.

(48) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; pp 187–191.

(49) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.

(50) (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (b) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.
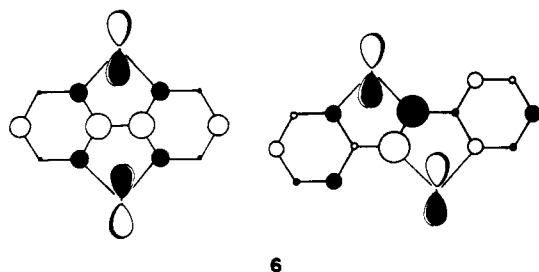
6

may thus provide valuable information as to whether direct or ligand-mediated metal–metal interaction prevails in binuclear complexes; this is a problem that has been much debated in connection with mixed-valence species.[50]

The unfavorable steric situation (3) in binuclear abpy complexes with six-coordinate metal centers merits two further comments: Tetrahedrally four-coordinate metal fragments such as $[CuL_2]^+$ should not encounter the difficulties (3) and are readily available.[51] Also, the preference of abpy for singly bidentate coordination allows us to synthesize tris abpy complexes such as $[Ru(abpy)_3]^{2+}$ without formation of coordination polymers; the latter occurs frequently in reactions of bppz or bptz with bifunctional metal fragments.[51]

9. Summary. In addition to the established[2d,5e,f,h,7] bpym system we have presented three other bis chelate ligands of the α-diimine type, which were formally constructed by insertion of a bifunctional π-electron-deficient group (pyrazine, tetrazine, azo group) between the pyridine rings of the prototypical α-diimine ligand, 2,2′-bipyridine.[52] In view of their various potential applications for the purposes mentioned in the Introduction, the calculational and experimental results obtained for the ligands and their coordination compounds with the paradigmatic π-electron-rich metal fragments $M(CO)_4$ (M = Cr, Mo, W) allow the following general characterizations:

Bpym and bppz have rather similar ligand effects in their complexes; while their nucleophilicity is still sufficient to coordinate with rather weak metal electrophiles, they have rather low LUMO levels that are lowered further by double coordination. Both ligands have relatively low-lying SLUMO levels with appreciable coordination activity ($\sum c_N^2$ values); binuclear bpym complexes are distinguished by their high symmetry and by a relatively small metal–metal distance with possible direct overlap of extended metal d orbitals.

Bptz and abpy ligands are rather weak σ donors despite the presence of pyridine "supporting" groups; however, the extraordinary feature of these two systems is their extremely low-lying LUMO level, which undergoes even further stabilization by metal coordination. Abpy exhibits the stronger response to coordinative perturbation so that binuclear complexes of abpy have more positive reduction potentials than those of bptz—in contrast to the situation found for the free ligands. Whereas bptz complexes still show a very weak second MLCT band because of a low-lying SLUMO, the binuclear abpy complex (μ-abpy)$[Mo(CO)_4]_2$ is quite unique in displaying a large gap between the first intense MLCT band in the near-IR region and the next detectable absorption maximum in the UV region; this unusually large LUMO/SLUMO difference is supported by MO calculations. Other extraordinary features of binuclear abpy complexes include an unusually short metal–metal distance for molecule-bridged coplanar systems, small width and little solvatochromism[10a] of the long-wavelength MLCT band (which indicates relatively small geometry changes between the ground and relaxed MLCT excited state), well-resolved yet closely spaced carbonyl stretching bands

in the vibrational spectrum of the $Mo(CO)_4$ binuclear complex (small k_i), and nonbonded interactions between the pyridine protons $H_{3,3'}$ and the equatorial substituents of six-coordinate metal centers. Mononuclear complexes of abpy avoid this situation by rotation of the free pyridyl ring (4) and must, therefore, undergo considerable conformational change (eq 4) to yield the binuclear systems. The formation of binuclear bptz complexes, on the other hand, requires only slight activation (eq 3); one very important asset of singly reduced binuclear bptz species is the enormous anion radical stability constant $K > 10^{20}$ (eq 5) and the localization of spin at the four nitrogen centers in the central tetrazine ring. This localization (cf. Chart II) has proven to be an invaluable advantage for ESR spectroscopy, as has been shown in a recent study illustrating the localized reduction in a mixed polyazine complex of ruthenium(II):[53]

$$[(bpy)_2Ru(\mu\text{-}bptz)Ru(bpy)_2]^{4+} \xrightarrow{+e^-}$$
$$[(bpy)_2Ru(\mu\text{-}bptz^{\bullet-})Ru(bpy)_2]^{3+} \quad (6)$$
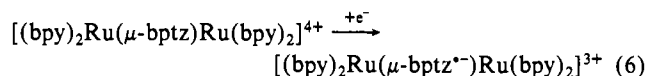
Being complementary in many ways, the two ligands abpy and bptz are members of a very special class of "noninnocent" ligands,[54] which offer extremely low lying π^* orbitals for interaction with occupied transition-metal d levels; related well-established ligands of this kind are the *o*-quinones.[55] The additional ability of abpy and bptz to act as binucleating bridging ligands, however, constitutes a particularly attractive combination in view of the need for such components in the various current areas of coordination chemistry as outlined in the Introduction.[1–6] With the experience gathered in this and other studies,[9] the calculational approach will be extended to a more comprehensive evaluation of existing systems,[5,56,57] to the design and computational screening of new binucleating ligands.[56b]

Registry No. bpym, 34671-83-5; bppz, 54266-39-6; bppz⁻, 105457-70-3; bppz²⁻, 105457-71-4; bptz, 1671-87-0; bptz⁻, 103711-41-7; bptz²⁻, 105457-72-5; abpy, 4109-58-4; abpy⁻, 103833-09-6; abpy²⁻, 105457-73-6; (μ-bppz)[Cr(CO)$_4$]$_2$, 105472-45-5; (μ-bppz)[W(CO)$_4$]$_2$, 105472-46-6; (bptz)Cr(CO)$_4$, 105472-47-7; (bptz)Mo(CO)$_4$, 102913-73-5; (abpy)-Mo(CO)$_4$, 102869-02-3; (bpym)Mo(CO)$_4$, 81986-02-9; (bpym)[Mo-(CO)$_4$]$_2$, 81986-03-0; (bppz)[Mo(CO)$_4$]$_2$, 102869-01-2; (bptz)[Mo-(CO)$_4$]$_2$, 97374-20-4; (bptz)[W(CO)$_4$]$_2$, 97374-21-5; (abpy)[Mo(CO)$_4$]$_2$, 97374-25-9; (bppz)[Cr(CO)$_4$]$_2^-$, 105472-49-9; (bppz)[Mo(CO)$_4$]$_2^-$, 105472-50-2; (bppz)[W(CO)$_4$]$_2^-$, 105472-51-3; (bptz)Cr(CO)$_4^-$, 105472-52-4; (bptz)Mo(CO)$_4^-$, 105472-53-5; (bptz)[Mo(CO)$_4$]$_2^-$, 103694-19-5; (bptz)[W(CO)$_4$]$_2^-$, 103694-20-8; (abpy)Cr(CO)$_4^-$, 105472-54-6; (abpy)Mo(CO)$_4^-$, 105472-55-7; (abpy)[Mo(CO)$_4$]$_2^-$, 103694-23-1; (bppz)[Cr(CO)$_4$]$_2^{2-}$, 105472-56-8; (bppz)[Mo(CO)$_4$]$_2^{2-}$, 105472-57-9; (bppz)[W(CO)$_4$]$_2^{2-}$, 105472-58-0; (abpy)[Mo(CO)$_4$]$_2^{2-}$, 105501-03-9; (THF)Cr(CO)$_5$, 15038-41-2; (THF)W(CO)$_5$, 36477-75-5; (nbd)Mo(CO)$_4$, 12146-37-1; (nbd)Cr(CO)$_4$, 12146-36-0; (abpy)Cr-(CO)$_4$, 105472-48-8; (bpym)[Mo(CO)$_4$]$_2^-$, 82532-99-8.

(51) Kohlmann, S.; Ernst, S.; Kaim, W., to be submitted for publication.
(52) McWhinnie, W. R.; Miller, J. D. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 135.

(53) Kaim, W.; Ernst, S.; Kohlmann, S.; Welkerling, P. *Chem. Phys. Lett.* **1985**, *118*, 431.
(54) Jørgensen, C. K. *Oxidation Numbers and Oxidation States*; Springer-Verlag: Berlin, 1969; p 291.
(55) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.
(56) Cf.: (a) Ghedini, M.; De Munno, G.; Denti, G.; Lanfredi, A. M. M.; Tiripicchio, A. *Inorg. Chim. Acta* **1982**, *57*, 87. (b) Ernst, S. Ph.D. Thesis, University of Frankfurt, 1987. (c) Morgan, R. J.; Fuchs, Y.; Lofters, S.; Strekas, T. C.; Gafney, H. D.; Baker, A. D. *Abstracts of Papers*, 191st National Meeting of the American Chemical Society, New York; American Chemical Society: Washington, DC, 1986; INOR 138.
(57) Kaim, W.; Kohlmann, S.; Ernst, S.; Olbrich-Deussner, B.; Bessenbacher, C.; Schulz, A. *J. Organomet. Chem.*, in press.