Coordination Characteristics of Four Isomeric α-Diimine Ligands. π Molecular Orbital Perturbation Calculations for the Bidiazines and Their Correlation with the Properties of Group 6 Metal Carbonyl Complexes[†]

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Abstract: Energies and charge distributions of the lower unoccupied π molecular orbitals have been determined for the isomeric bidiazine ligands 3,3'-bipyridazine (bpdz), 4,4'-bipyrimidine (bpm), 2,2'-bipyrazine (bpz), and 2,2'-bipyrimidine (bpym) as well as for 2,2'-bipyridine (bpy) by Hückel MO perturbation calculations. In conjunction with experimental pK_a values, the calculation results are related to the different stabilities, redox potentials, and various spectroscopic properties of chromium, molybdenum, and tungsten tetracarbonyl complexes with these ligands. Pentacarbonyltungsten complexes were isolated as intermediates in the reactions between W(THF)(CO)$_5$ and bpdz or bpm. Each of the four isomeric ligands exhibits very characteristic features, and the potential uses of the individual systems for different purposes in coordination chemistry are discussed. While bpdz is the strongest base in that series, thus compensating for a rather high-lying π* level, the bpm complexes exhibit the strongest back-bonding interaction because of a very low-lying π* level and sufficient ligand basicity. The bpz system is distinguished by acquiring high amounts of additional charge at both sets of nitrogen centers upon reduction, and finally, the otherwise less outstanding bpym ligand is unique among the bidiazine isomers by forming binuclear bis-chelate complexes on second coordination.

Heterocyclic α-diimine ligands such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) have found extensive application in analytical and preparative coordination chemistry[1,2] for almost a century.[3] The recent focus on coordination compounds such as [Ru(bpy)$_3$]$^{2+}$ with special redox[4] and photocatalytic properties[5] has triggered a search for related ligands with deliberately modified chemical and physical behavior; this search has included ring substitution at the classical bpy and phen systems[6] and their incorporation in greater π systems.[7] Since the replacement of CH by N in such systems leads to more π-electron-deficient compounds, there have also been efforts to use coupled diazines (pyridazines, pyrimidines, and pyrazines) instead of the coupled pyridine bpy as chelate ligands; there are four possible symmetrically coupled bidiazines with the α-diimine structure: 3,3'-bipyridazine (bpdz), 4,4'-bipyrimidine (bpm), 2,2'-bipyrazine (bpz), and 2,2'-bipyrimidine (bpym) (Chart I).

Whereas 2,2'-bipyrimidine has been widely employed recently, especially since it may also form binuclear molecule-bridged complexes,[8] the 2,2'-bipyrazine system was introduced by Crutchley and Lever[9] as a promising π-acceptor ligand for π-electron-rich d[6] metal fragments such as Ru(II), Mo(0), and W(0); however, the low basicity typical for such 1,4-diazines reduces the back-bonding capability of bpz despite its favorable π-acceptor level.[9b] Both the bpym[10a] and bpz[10b] ligands have become commercially available in the meantime. As concerns the other two isomers bpdz and bpm, the complex [Ru(bpdz)$_3$]$^{2+}$ was studied by Tazuke and co-workers as was a similar complex with 6,6'-dimethyl-4,4'-bipyrimidine;[11] however, there was no other coordination chemistry reported with these two ligands except for some experiments with Fe^{2+} in aqueous solution.[12]

Guided by theoretical concepts and calculations,[13] we have now undertaken a comparative spectroscopic and electrochemical study

Chart I

bpdz

bpm

bpz

bpym
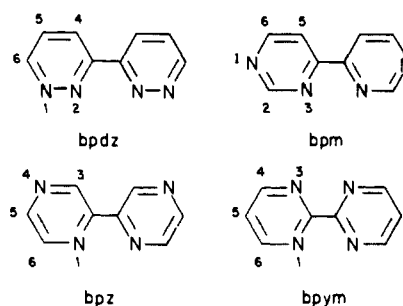
of the coordination properties of the four bidiazines in Chart I using tetracarbonylchromium, -molybdenum, and -tungsten as

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metal fragments.

Experimental Section

The bidiazines bpdz[12] and bpz[9b] were synthesized according to literature procedures; for 4,4'-bipyrimidine (bpm) the method of Effenberger[14] proved to be superior to that of Lafferty and Case[12] in order to prepare larger quantities of the ligand.

pK_a values of bpdzH[+] and bpmH[+] were determined according to the procedure described by Crutchley and Lever[9c] at ligand absorption maxima of 260 (bpdz) and 276 nm (bpm); the protonation medium was sulfuric acid in the concentration range 0.005–0.75%. The concentrations of the bases were 3.2×10^{-5} (bpdz) and 8.05×10^{-5} mol/L; the values pK_{a_1} (bpdz-H^{+}) = 3.37 and pK_{a_1} (bpm-H^{+}) = 1.50 were obtained by standard analysis methods[9c] and are believed to be correct within ±0.25.

All coordination compounds were synthesized and studied under an atmosphere of dry argon using dried solvents. Chromatographic separation was carried out with increasingly polar solvents on Florisil (Merck) columns.

Mo(bpym)(CO)₄ was prepared according to the literature.[8d]

Mo(bpz)(CO)₄ and W(bpz)(CO)₄ were synthesized in a thermal reaction between the ligand and hexacarbonylmetal;[9b] however, the chromium derivative could not be obtained via this route. We have, therefore, employed the photolytically generated pentacarbonylmetal–THF complexes[15,16] as activated starting materials; a typical reaction runs as follows:

Cr(bpz)(CO)₄. Cr(CO)₆ (0.33 g, 1.5 mmol) was converted to the solvent complex Cr(THF)(CO)₅ by irradiation in 70 mL of tetrahydrofuran. Addition of 200 mg (1.27 mmol) of bpz and warming up to 35 °C resulted in slow CO evolution while the solution turned blue. The reaction was stopped after 8 h, the solvent was removed, and the residue was chromatographed on Florisil. The blue zone of Cr(bpz)(CO)₄ was collected, and rapid crystallization from hexane/ether afforded thermolabile dark-blue crystals (60 mg, 19%).

The tetracarbonylmetal(bpdz) and -(bpm) complexes were prepared similarly; however, in all these cases we could observe yellow-to-red intermediates which are presumably the mono- and bis(pentacarbonylmetal) complexes with coordination occurring at the less-hindered peripheral nitrogen centers. For M = W we have isolated these intermediates and confirmed their identity spectroscopically:

(*μ-N¹,N¹'-bpm*)[W(CO)₅]₂. W(CO)₆ (0.53 g, 1.5 mmol) was converted to W(THF)(CO)₅ in 70 mL of THF and added to 100 mg (0.63 mmol) of bpm. Stirring at low temperatures (−15 °C) first yielded the labile mononuclear complex W(*N¹-bpm*)(CO)₅; after 24-h reaction time at room temperature, a dark precipitate was collected and chromatographed on Florisil. The dark-red zone eluted with hexane/toluene was collected: stable red crystals (10%). Anal. C, H, N.

W(*N¹-bpdz*)(CO)₅ and (*μ-N¹,N¹'-bpdz*)[W(CO)₅]₂ were obtained similarly as yellow and orange compounds, respectively: yields 5% and 15%. Anal. C, H, N.

The reaction conditions to obtain the tetracarbonyl complexes from M(THF)(CO)₅ and the ligands via the pentacarbonylmetal intermediates in THF are described in the following; chelate complexes of bpdz were found to crystallize as rather stable monotetrahydrofuranates from hexane/THF.

Cr(bpdz)(CO)₄: 3-h reflux, yield of pure compound 64%, copper-colored crystals. Anal. C, H, N.

Mo(bpdz)(CO)₄. Due to the incomplete photolytic conversion of Mo(CO)₆ to Mo(THF)(CO)₅,[17] the metal component was used in four-
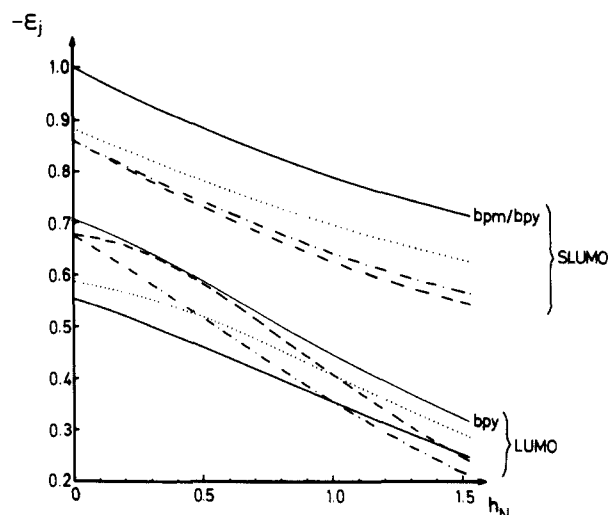

Figure 1. Correlation diagram of LUMO (b₂ᵤ) and SLUMO (a₂) energies from HMO perturbation calculations for bpy (—), bpdz (- - -) (—), bpz (-·-·), and bpym (···) vs. the Coulomb integral parameter h_N at the α-diimine nitrogen centers (noncoordinating nitrogen centers: $h_{N'}$ = 0.5).

fold excess. Reaction time was 2 days at room temperature; prior to chromatographic purification, excessive Mo(CO)₆ was removed by rapid recrystallization from THF/hexane: stable maroon crystals (49%). Anal. C, H, N.

W(bpdz)(CO)₄: 3 days of reflux in THF to obtain the tetracarbonyl in 34% yield; dark-brown crystals. Anal. C, H, N.

Cr(bpm)(CO)₄. Rapid disappearance of the red-colored intermediate and formation of the blue chelate complex were observed. After stirring overnight at room temperature, the mixture was worked up as described above: thermolabile dark-blue crystals, yield 31%.

Mo(bpm)(CO)₄. The red intermediate is observed for some minutes after combining bpm and Mo(THF)(CO)₅ at room temperature; removal of excess Mo(CO)₆ and chromatography yielded stable brown crystals (43%). Anal. C, H, N.

W(bpm)(CO)₄. At room temperature, the reactants W(THF)(CO)₅ and bpm form the red binuclear complex (vide supra). Conversion to the tetracarbonyltungsten chelate species requires refluxing for several hours in THF: stable dark crystals (22%). Anal. C, H, N.

Instrumentation. ¹H NMR: Bruker WH 270 and Varian A 60, solvent or TMS as internal standard. IR: Perkin-Elmer 283B, solution spectra in THF. UV/vis: Pye-Unicam SP 1800. Cyclic voltammetry: PAR system 173/175, glassy carbon working electrode, satured calomel reference electrode (SCE), 0.1 M solutions of tetrabutylammonium perchlorate in dry dimethylformamide (DMF) or acetonitrile as electrolyte. Concentration of complexes during measurement was about 10⁻³ M, 100 mV/s scan rate.

Elemental analyses were performed in the laboratory of Prof. W. Ried, University of Frankfurt; Hückel MO calculations were carried out by using the available program on a VAX 750/11 system.

Results and Discussion

1. π Molecular Orbital Energies of 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 σ-donor strength.[9b] Although both of these components interact synergistically in the complexes via "back-bonding", we start with a separate consideration of these ligand properties.

A number of molecular orbital (MO) calculations has already been performed for some of the α-diimine systems in Chart I with regard to charge distributions,[18] conformations, and ionization energies;[19] however, no approach has been made yet to evaluate the π-acceptor properties of all four bidiazines in comparison to

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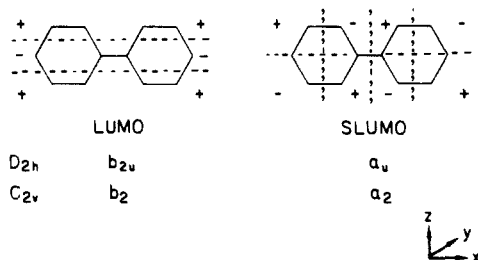
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Chart II

LUMO   SLUMO

D_{2h} b_{2u} a_u

C_{2v} b_2 a_2

2,2'-bipyridine. Therefore, we have carried out Hückel molecular orbital (HMO)[20] calculations for these five systems (Chart I); Figure 1 shows orbital energy correlations of the respective lowest unoccupied molecular orbital (LUMO) and second lowest unoccupied molecular orbital (SLUMO), depending on the Coulomb integral parameter h_N for the coordinating (α-diimine) nitrogen centers. The noncoordinating N centers have $h_{N'} = 0.5$ so that $h_N = h_{N'} = 0.5$ illustrates the situation for the free ligand; coordination of an electrophilic metal fragment may then be reproduced by an increase of the Coulomb integral at the coordination site.[21]

In agreement with the electronegative character of nitrogen relative to CH, all bidiazines have LUMO energies more positive than $\epsilon_{LUMO}(bpy)$, albeit with considerable differences. For the free ligands ($h_N = 0.5$) and their complexes with uncharged species, a value of $h_N < 1$ is reasonable, and in that range it is the bpm ligand and not the bpz isomer which exhibits maximum LUMO stabilization. This result could not be easily anticipated since pyrazine is definitely a better π acceptor than pyrimidine;[12] however, it seems that the presence of nitrogen centers in the 4,4'-position, the "para" position of the perturbed biphenyl π system, has a particularly strong effect in stabilizing the LUMO. For the other three bidiazines, the sequence of the LUMO energy is $\epsilon(bpz) > \epsilon(bpym) > \epsilon(bpdz)$ in the region $0.5 < h_N < 1.0$.

The cyclovoltammetrically determined reduction potentials of the ligands (section 7, Table III) show that such a sequence is in good agreement with experimental values, except for the fact that the bpdz ligand (containing N–N linkages) is found to be slightly more reducible than would be anticipated from the HMO calculations.

Looking at the second lowest molecular orbital (SLUMO) energies (Figure 1), which are relevant, for example, for the assignment of higher-energy metal-to-ligand charge-transfer (MLCT) absorption bands,[9b] a totally different sequence emerges. Whereas both the bpdz and bpz systems have rather positive SLUMO energies, the bpm ligand has now the same negative SLUMO energy as the bpy system; bpym takes an intermediate position (Figure 1).

The identical SLUMO behavior of bpm and bpy has its origin in the nodal properties of the orbitals in the parent 12 center "biphenyl" π system. While the LUMO (b_{2u}) has nodal planes through "bonds" only (Chart II), the SLUMO of that system (a_u) has a nodal plane through the connecting centers and through the 4,4'-(para)-positions; hence, there is no difference between bpy and bpm (=5,5'-N_2bpy) with respect to the SLUMO.

It is interesting to note that bpm has the most negative SLUMO and the most positive LUMO energy among the four bidiazines ($\Delta\epsilon = 0.424$ at $h_N = 0.5$); on the other extreme, bpdz displays the smallest LUMO/SLUMO difference among the ligands in Chart I with $\Delta\epsilon = 0.150$ at $h_N = 0.5$; thus, the hitherto least studied isomers show the most pronounced effects. The accessibility of the ligand SLUMO in relation to the ligand LUMO may become important in the modifying of excited state properties of such charge-transfer complexes.[5]

2. Basicities of the Neutral Ligands. Effective back-bonding with α-diimine ligands requires, besides a low-lying LUMO, sufficient σ-donor capacity via the coordinating nitrogen centers. Frequently, both of these effects run oppositely to each other; for instance, Crutchley and Lever have pointed out[9b] that the stabilization of the π^* orbital of bpz relative to bpy is compensated by the poorer σ-donor strength of this 1,4-diazine[22] ligand. An approximate measure of the σ donor strength is the pK_a values of the conjugate acids, i.e., the equilibrium constants for complexation with H^+, which are p$K_{a_1} = 4.45$[23] for bpy and p$K_{a_1} = 0.45$ for bpz.[9c] We have similarly determined the first pK_a values for the two less used ligands bpdz (p$K_{a_1} = 3.37$) and bpm (p$K_{a_1} = 1.50$), both of which are stronger bases than bpz.[24] Although this result is in agreement with the general sequence for the parent diazines (pK_{a_1}(pyridazine) $= 2.24 >$ pK_{a_1}(pyrimidine) $= 1.23 >$ pK_{a_1}(pyrazine) $= 0.51$),[25] it nevertheless means that bpm has the lowest lying π^* level without being the poorest σ donor in the bidiazine series and should thus represent a very promising π-acceptor ligand.[13a] On the other hand, the suprisingly high pK_a of bpdzH$^+$ also suggests strong back-bonding of the neutral ligands toward π electron-rich metal fragments,[13b] an additional bonus being the improved dissociative stability of (bpdz)ML$_x$ complexes.

3. Estimation of Basicity Changes on Reduction. Another factor which may determine the redox properties, and in particular, the stability of the reduced complexes, is the σ-donor strength of the anion radical ligands. Pulse radiolysis studies have recently demonstrated that the basicity of the heterocyclic α-diimine ligands bpy and phen increases by about 20 orders of magnitude upon one-electron reduction.[26] As an approximate measure for the relative σ-basicity changes on going from the neutral to the reduced ligand, one may use the squared Hückel π MO coefficients c^2 at the coordinating centers.[27] Starting from eq 1[20] where q_π is the

$$\delta[E_\pi(base) - E_\pi(acid)] = q_\pi(h_N - h_{N^+})\beta \qquad (1)$$

π-charge order, h_N and h_{N^+} are the Coulomb integral parameters for base and acid, and β is the Hückel MO resonance integral, one arrives at eq 2[27a] when considering only the relative basicity changes between the neutral and the reduced state of the system.

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

In eq 2, μ denotes the level additionally occupied in the anion. The significance of such calculations had been demonstrated recently in a study of reduced bpy and phen systems;[21b] for 1,10-phenanthroline, simple MO methods predict a MO (a_2) with very small N coefficients as the LUMO,[28] whereas ESR experiments show clearly that the added electron rather occupies the nearby b_1 orbital with large coefficients at the coordinating nitrogen centers.[21b]

For the bpy and bidiazine LUMOs, we obtained ($h_N = h_{N'} = 0.5$) $c_N^2(bpy) = 0.138$, $c_N^2(bpdz) = 0.163$, $c_N^2(bpm) = 0.104$, $c_N^2(bpz) = 0.170$, and $c_N^2(bpym) = 0.095$. Values for the SLUMO which may be of interest when looking at higher-energy MLCT transitions are $c_N^2(bpy, bpm) = 0.106$, $c_N^2(bpdz) = 0.118$, $c_N^2(bpz) = 0.110$, and $c_N^2(bpym) = 0.095$; note that the SLUMO of the bpym *ligand* (D_{2h}) is twofold degenerate (b_{3g}, a_u). The data

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for the LUMOs predict that coordination compounds of reduced bpdz and bpz may receive some additional stabilization, especially in comparison with the bipyrimidines bpm and bpym. These calculation results are of particular significance for the bonding situation in metal-to-ligand charge-transfer (MLCT) excited states of metal complexes with such ligands, because these states are usually formulated as containing anion radical ligands (eq 3). The

$$(\alpha\text{-diimine})M^nL_x \xrightarrow{h\nu} [(\alpha\text{-diimine}^-\cdot)M^{(n+1)}L_x]^* \quad (3)$$
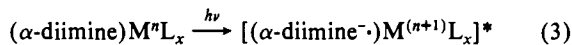
comparatively strong increase of the basicity of the anion radicals in the cases of bpdz and bpz may thus be used[27a] to explain the rather long lifetimes of the MLCT excited states in corresponding tris(ligand)ruthenium(II) complexes.[9a,11] Another pertinent result from these calculations is an estimate concerning the relative basicity increase at the peripheral nitrogen centes N' in chelate complexes after occupation of the first π^* level. This kind of reactivity is exemplified, for example, by the use of bpym as binucleating ligand[8] or by the studies by Lever and co-workers on the additional coordination of electrophiles such as H^+,[9c,8h] BF_3,[9h] Ag^+, or $[Fe(CN)_5]^{2+}$ [9i] to the $N_{4,4'}$ centers in MLCT excited bpz complexes. Our calculations at $h_N = 1.0$ show that bpz and bpm should be favored ($c_{N'}^2 = 0.096$) in this respect relative to the bpdz and bpym systems ($c_{N'}^2 = 0.056$).

4. Synthesis of Complexes. α-Diiminetetracarbonyl complexes of group 6 d metals may be prepared from hexacarbonylmetals $M(CO)_6$ via thermal[9b] or photochemical[15] activation. Since the (bidiazine)tetracarbonylchromium complexes proved to be rather thermolabile and because photoreactivity of the ligands or of the complexes could not be ruled out, we used a mild procedure to prepare the complexes, viz., thermal THF and CO substitution at photogenerated $M(THF)(CO)_5$ complexes (eq 4). For the bpdz

(4)
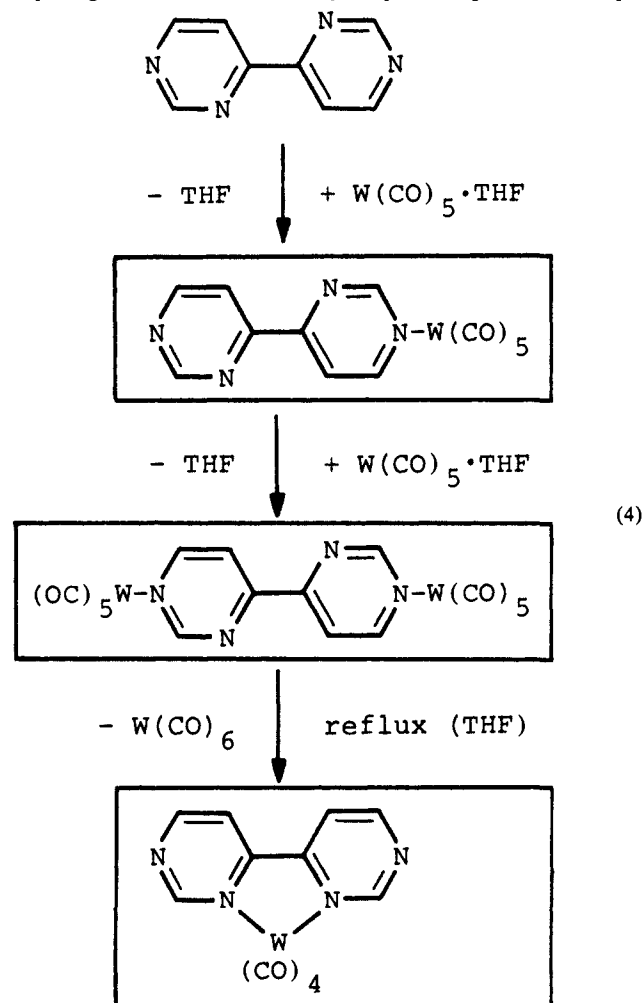
and bpm systems, these reactions were found to proceed stepwise by first forming pentacarbonylmetal complexes;[13a] similar, more

short-lived species were found in the photoreactions of $W(CO)_6$ with other α-diimines, including 2,2'-bipyridines.[29,30] For the bidiazines, an additional complication arises by $M(CO)_5$ coordination to the sterically better available non-α-diimine nitrogen centers, and in the case of the bpm and bpdz tungsten carbonyl systems, we have tried and succeeded to isolate such intermediates, the mono- and binuclear complexes with $W(CO)_5$ coordinated to the peripheral N atoms. The pentacarbonyltungsten complexes of bpm are related to the mono- and binuclear pentacarbonyltungsten complexes[31] of the bridging ligand 4,4'-bipyridine (bp) which has no σ-donor centers available for chelate coordination.

bp
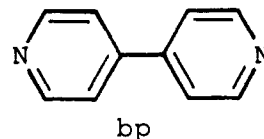
The binuclear compounds $W_2(bpm)(CO)_{10}$ and $W_2(bpdz)$-$(CO)_{10}$ are kinetically stable and may be conveniently handled at room temperature; they are converted to the thermodynamically favored tetracarbonyl chelate compounds and $W(CO)_6$ only after prolonged refluxing in THF (eq 4).

5. ^1H NMR Spectra. The ligands and complexes display rather simple proton NMR spectra of the ABC type because the six-membered rings are equivalent in either the cis form (chelate complexes) or in the trans configuration; the latter is probably preferred by the non-chelate species $W_2(bpm)(CO)_{10}$ and W_2-$(bpdz)(CO)_{10}$ and by the ligands.[19] Assignments of resonances were made according to the coupling pattern and according to the expected coupling constants;[32] furthermore, a relative low-field shift has been attributed to those protons adjacent to the non-coordinated nitrogen centers (Table I). Assignments for Cr-$(bpz)(CO)_4$ were made according to the suggestions of Crutchley and Lever.[9b]

6. Carbonyl Vibrational Spectra. In their infrared spectra, the tetracarbonylmetal complexes of the bidiazine ligands display four carbonyl stretching bands, of which the two central features show frequently overlapping (Table II). Although CO stretching frequencies and, in particular, calculated force constants provide very useful information on the ground-state acceptor properties of coligands,[9b] the differences within the series of bidiazine complexes are relatively small, for example, in comparison to the strong effects observed with α-diimine complexes containing the azo group.[33,34]

For the pentacarbonyltungsten complexes of bpdz and bpm, the expected pattern of three bands (A_1, E_1, and A_1) is observed (Table II); together with the ^1H NMR data and elemental analysis results, these CO stretching frequencies provide conclusive evidence for the formulation of these intermediates (eq 4).

7. Redox Potentials. In order to obtain comparable electrochemical data, we have studied all the bidiazine ligands and their complexes by cyclic voltammetry in N,N-dimethylformamide (DMF) solutions (Figures 2 and 3; Table III).

A number of electrochemical data has already been reported for bpdz,[11] bpm,[35] bpz,[9b,9d,36] and bpym;[37] however, the conditions of measurement had been quite different. One such difference

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Table I. ¹H NMR Data of New Bidiazine Tetracarbonylmetal Complexes[a]

compd	solvent	$\delta_{H_{2,2'}}$	$\delta_{H_{3,3'}}$	$\delta_{H_{4,4'}}$	$\delta_{H_{5,5'}}$	$\delta_{H_{6,6'}}$	$J_{4,5}$	$J_{5,6}$	$J_{4,6}$
bpdz	$CDCl_3/Me_2SO\text{-}d_6$			8.71	7.77	9.27	8.5	4.5	1.8
(bpdz)Cr(CO)₄	$Me_2CO\text{-}d_6$			8.75	7.99	9.23	8.6	4.9	1.5
(bpdz)Mo(CO)₄	$Me_2CO\text{-}d_6$			8.88	8.09	9.29	8.7	4.9	1.6
(bpdz)W(CO)₄	$Me_2CO\text{-}d_6$			8.93	8.11	9.72	8.7	4.9	1.7
(bpdz)W(CO)₅	$Me_2CO\text{-}d_6$			8.54	8.07	9.17	~8.7	~5.0	~1.5
				8.76	8.22	9.29			
(bpdz)[W(CO)₅]₂	$Me_2CO\text{-}d_6$			8.70	8.07	9.78	8.7	5.5	1.3
bpm	$CDCl_3$	9.36			8.43	8.91		5.1	
(bpm)Cr(CO)₄	$CDCl_3$	9.81			8.67	9.14		5.1	
(bpm)Mo(CO)₄	$CDCl_3$	9.74			8.75	9.20		5.2[c]	
(bpm)W(CO)₄	$CDCl_3$	9.86			8.82	9.22		5.3[d]	
(bpm)[W(CO)₅]₂	C_6D_6	8.87			7.12	7.96		5.7	
bpz[b]	$Me_2SO\text{-}d_6$		9.53		8.84	8.84			
(bpz)Cr(CO)₄	$Me_2CO\text{-}d_6$		9.83		8.74	9.29		3.4[e]	

[a] From 60-MHz (ligands) and 270-MHz spectra (complexes); coupling constants J in hertz. [b] Reference 9b. [c] $J_{2,5}$ = 1.2 Hz. [d] $J_{2,5}$ = 0.8 Hz. [e] $J_{3,6}$ = 1.3 Hz.

Table II. CO Vibrational Stretching Frequencies ν_{CO} [cm⁻¹] of (α-Diimine)carbonylmetal Complexes[a]

complex	tetracarbonyls			
	A_1 (s)	B_1 (vs)	A_1 (sh)	B_2 (s)
(bpy)Mo(CO)₄	2010	1905	1888	1845
(bpdz)Cr(CO)₄	1998	1900 (br)	1900 (br)	1865
(bpdz)Mo(CO)₄	2001	1900 (br)	1900 (br)	1862
(bpdz)W(CO)₄	2000	1893 (br)	1893 (br)	1860
(bpm)Cr(CO)₄	2000	1905 (br)	1905 (br)	1855
(bpm)Mo(CO)₄	2010	1908	1895	1850
(bpm)W(CO)₄	2000	1900 (br)	1900 (br)	1850
(bpz)Cr(CO)₄	2005	1915 (br)	1915 (br)	1860
(bpz)Mo(CO)₄	2018	1920	1910	1860
(bpz)W(CO)₄	2018	1927	1905	1857
(bpym)Mo(CO)₄	2012	1905	1890	1845

complex	pentacarbonyls		
	A_1 (w)	E_1 (vs)	A_1 (s)
(bpdz)W(CO)₅	2055	1925	1895
(bpdz)[W(CO)₅]₂	2055	1925	1895
(bpm)W(CO)₅	2070	1935	1907
(bpm)[W(CO)₅]₂	2065	1935	1905

[a] In THF solution, except for (bpz)W(CO)₄.[9b]

Table III. Redox Potentials of Bidiazine Ligands and of Their Carbonylmetal Complexes[a,b]

compd	$E_{ox}^{(+/0)}$	$E_{red}^{(0/-)}$	$E_{red}^{(-/2-)}$
bpy[c]		-2.18	-2.68 (i)[b]
(bpy)Mo(CO)₄	+0.82 (i)	-1.40	-2.15 (i)
bpdz		-1.72	-2.07 (i)
(bpdz)Cr(CO)₄	+0.51	-1.19	-2.05 (i)
(bpdz)Mo(CO)₄	+0.70 (i)	-1.09	-1.93 (i)
(bpdz)W(CO)₄	+0.70 (i)	-1.04	-1.85 (i)
(bpdz)[W(CO)₅]₂	+1.02 (i)	-0.90	
bpm		-1.34	-2.02 (q)
(bpm)Cr(CO)₄	+0.64	-0.80	-1.56 (q)
(bpm)Mo(CO)₄	+0.86 (i)	-0.71	-1.45 (q)
(bpm)W(CO)₄	+0.86 (i)	-0.68	-1.39
(bpm)[W(CO)₅]₂	+1.01 (i)	-0.67	-1.35 (i)
bpz[c]		-1.66	-2.38
(bpz)Cr(CO)₄	+0.68	-1.09	-1.53 (i)
(bpz)Mo(CO)₄	+0.90 (i)	-0.89	-1.67 (i)
(bpz)W(CO)₄	+0.90 (i)	-0.83	-1.45 (i)
bpym		-1.73	-2.44 (i)
(bpym)Mo(CO)₄	+0.84 (i)	-1.07	-1.71 (i)

[a] Data from cyclic voltammetry, potentials in volts vs. SCE. Solvent: DMF; reduction potentials in CH_3CN are more negative by about 0.2 V. [b] (i) denotes irreversible redox processes with peak potentials given (scan rate 100 mV/s); (q) denotes a quasi-reversible redox process. [c] Low-temperature data from ref 36.

Figure 2. Cyclovoltammogram of (bpm)W(CO)₄ between 0 and -2.0 V vs. SCE in DMF/0.1 M $Bu_4N^+ClO_4^-$.
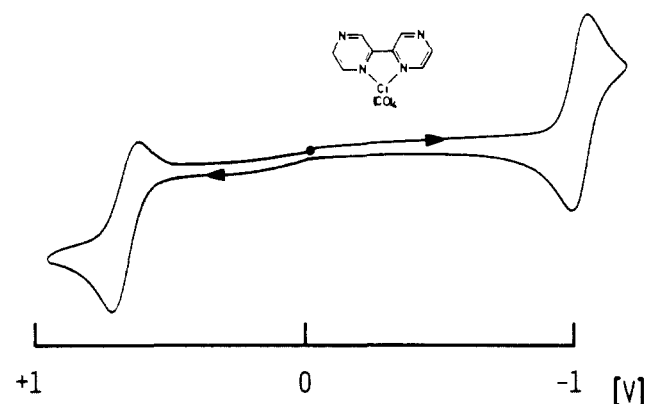

Figure 3. One-electron oxidation and reduction of (bpz)Cr(CO)₄ as illustrated by cyclovoltammograms between +0.95 and -1.20 V vs. SCE (electrolyte: DMF/0.1 M $Bu_4N^+ClO_4^-$).

concerns the solvent; our studies have shown that reduction potentials obtained in DMF are 0.1–0.2 V more positive than those measured in acetonitrile.

When comparing the bidiazine ligands, they all exhibit quite reversible (ΔE = 60–80 mV) first reduction waves in their cyclovoltammograms, followed by irreversible second reduction steps. 4,4'-Bipyrimidine (bpm) is by far the most easily reduced isomer, whereas the bpz, bpdz, and bpym ligands have rather similar

potentials, still much more positive than that of bpy. Although this sequence agrees qualitatively with the calculated LUMO energies (Figure 1), the individual differences are apparently reproduced less exactly.

Turning to the metal tetracarbonyl complexes, there is a clear and established[38] order in that the chromium species have the most negative reduction potential for a given α-diimine ligand system

(38) Cf.: tom Dieck, H.; Kühl, E. *Z. Naturforsch., B* **1982**, *37b*, 324.

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while the tungsten derivative is most easily reduced. A comparison of the different bidiazine complexes of a given metal fragment reveals the persistence of the sequence found for the ligands albeit with some modifications. Bpm complexes are again most easily reduced, followed by the bpz, bpdz, and bpym complexes, in that order. The differentiation among the complexes may reflect the different increase in basicity of the reduced ligand according to the estimation given in section 3.; reduced bpz and also bpdz complexes will receive a particular stabilization by that mechanism. A correlation between the reduction potentials of the ligands and of their respective metal tetracarbonyl complexes also illustrates the influence of ligand basicity in the ground and reduced states; bpdz, bpm, and bpz exhibit relatively large shifts of about 0.55 (Cr) and 0.6–0.7 V (Mo, W) toward positive potentials upon complexation. The somewhat smaller thermodynamic stabilization of (α-diimine)Cr(CO)₄ anion radical complexes was recently demonstrated in the bpy series.[39] A second reversible reduction step after the first uptake of an electron has been observed only for some bpm complexes (Table III); the range of potential differences $E^{0/-} - E^{-/2-} \sim 0.5{-}0.8$ V corresponds to radical anion stability constants $K > 10^9$ according to eq 5. Detailed ESR and ENDOR studies of these persistent paramagnetic species will be the subject of a forthcoming report.[40]

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

In contrast to the generally reversible one-electron reductions of the ligands and complexes, the electrochemical oxidation in DMF is reversible only for the chromium tetracarbonyl complexes. This process corresponds to a loss of one electron from a metal-centered orbital (Cr⁰ → Cr¹); it is well-known that the +I oxidation state of molybdenum and tungsten tetracarbonyl complexes is rather labile.[38] Neither the increase of the scan rate up to 500 mV/s nor the use of the very little nucleophilic solvent CH₂Cl₂[38] did improve this situation; solubility problems prevented studies at low temperatures.[36] The bidiazine ligands are apparently not very suitable to accommodate organometallic fragments in higher oxidation states; nevertheless, the oxidation potentials of the Cr(CO)₄ complexes in Table III reflect nicely the effect of ground-state basicity of the ligands. Of the three new (bidiazine)Cr(CO)₄ complexes, the bpdz isomer is most easily oxidized, in agreement with the high pK_a of the ligand. Bpm and bpz complexes are oxidized at distinctly higher potentials, and in accordance with the relative pK_a values (section 2), it is the bpz complex which exhibits the highest oxidation potential and hence contains the most stabilized filled metal level. Similar results have been obtained using the Ru(III)/Ru(II) couple in [Ru(bidiazine)₃]ⁿ⁺ complexes as a probe for the effect of ligand basicity; there it is also the bpz complex which requires the highest oxidation potential.[13a]

A comparison between the binuclear pentacarbonyltungsten complexes of bpdz and bpm with their tetracarbonyltungsten analogues reveals that the reduction potentials are quite similar; the reversible nature of these processes is obvious from the cyclovoltammetry experiments (Table III) and from the ESR characterization of persistent anion radicals.[40] Apparently, double coordination of the relatively weak electrophiles W(CO)₅ to the peripheral nitrogen centers is almost equivalent to a chelate coordination of the stronger electrophilic W(CO)₄ fragment to the α-diimine nitrogen sites. However, there is a distinct difference in the anodic peak potentials resulting from irreversible oxidation of the two kinds of complexes (Table III); the pentacarbonyltungsten species have a more stabilized HOMO than corresponding W(CO)₄ species which also results in lower energy MLCT absorptions of the latter species.

8. MLCT Absorption Spectra. From the diffferences between the oxidation and reduction potentials (Table III), it is possible to estimate the energies of the first metal-to-ligand (π* ← d) charge-transfer transitions.[41a,42,43] Table IV shows the energies

Table IV. Metal-to-Ligand Charge-Transfer Absorption Maxima E_{CT} of (α-Diimine)carbonylmetal Complexes in Two Different Solvents[a]

complex	toluene		tetrahydrofuran	
	$E_{CT(1)}$	$E_{CT(2)}$	$E_{CT(1)}$	$E_{CT(2)}$
Tetracarbonyls				
(bpy)Cr(CO)₄[b]	2.32	c	2.45	c
(bpy)Mo(CO)₄[b]	2.49	c	2.63	c
(bpy)W(CO)₄[b]	2.39	c	2.54	c
(bpdz)Cr(CO)₄	1.98	2.69	2.11 (3.86)	2.82 (3.75)
(bpdz)Mo(CO)₄	2.14	3.06	2.25 (3.82)	3.12 (3.60)
(bpdz)W(CO)₄	2.09	2.82	2.21 (3.85)	2.99 (3.60)
(bpm)Cr(CO)₄	1.80	3.10	1.97 (3.46)	3.20 (3.67)
(bpm)Mo(CO)₄	1.97	3.26	2.14 (3.58)	3.40 (3.69)
(bpm)W(CO)₄	1.88	3.24	2.04 (3.67)	3.40 (3.75)
(bpz)Cr(CO)₄	2.06	3.00	2.15	3.18
(bpz)Mo(Co)₄	2.19	3.21	2.31 (3.84)	3.28 (3.76)
(bpz)W(CO)₄	2.14	3.16	2.25 (3.88)	3.35 (3.75)
(bpym)Cr(CO)₄	2.24[d]	3.07[d]	2.27 (3.43)[e]	3.09 (3.83)[e]
(bpym)Mo(CO)₄	2.37	3.25	2.53	3.30
(bpym)W(CO)₄	2.32[d]	3.25[d]	2.36 (3.62)[e]	3.28 (3.87)[e]
Pentacarbonyls				
(bpdz)W(CO)₅			3.1[f]	3.1[f]
(bpdz)[W(CO)₅]₂	2.82	3.10[g]	2.92 sh	3.10[g]
(bpm)W(CO)₅			2.95 sh	3.10[g]
(bpm)[W(CO)₅]₂	2.37	3.13[g]	2.70 (2.89)	3.13 sh[g]
(bp)[W(CO)₅]₂	2.83[h]	3.06[g,h]		

[a] 1 eV = 8066 cm⁻¹; log ε (ε in M⁻¹ cm⁻¹) given in parentheses. [b] From ref 45. [c] Obscured by π* → π transitions. [d] In benzene solution, ref 8i. [e] In dichloromethane solution, ref 8i. [f] Overlapping MLCT and LF (¹E ← ¹A) absorption bands. [g] Ligand-field (LF) transition (¹E ← ¹A). [h] In benzene solution, ref 31; bp = 4,4′-bipyridine.

of the first and second absorption bands of the bidiazine carbonylmetal complexes in two solvents of different polarity; for better comparison with electrochemical potentials, these energies are given in electronvolts.

Starting with the tetracarbonylmetal complexes, the first long-wavelength absorption band in such α-diimine chelate complexes has been shown to comprise several transitions from filled d levels to the unoccupied lowest π* level of the ligand, the dominating component being a symmetry-allowed $\pi_1^* \leftarrow d_{yz}$ transition.[44,45] The extinction coefficients of these bands typically range between 10³ and 10⁴ M⁻¹ cm⁻¹,[46] and such complexes are also known to display a distinctive negative solvatochromism[9f,41b] which results from the metal-to-ligand charge shift in the MLCT excited state and thus depends strongly on the extent of back-bonding interaction.[47,48]

In agreement with all the theoretical and experimental evidence presented so far, the lowering of the MLCT transition energy follows the order bpym > bpz ~ bpdz > bpm in corresponding M(CO)₄ complexes, as does the solvent sensitivity.[48] Somewhat surprisingly, the absorption energies of bpdz complexes are even slightly smaller than those of the bpz analogues, despite the lower π* level and more positive reduction potential of the latter system. However, the distinctly higher basicity of the bpdz ligand more than compensates for this disadvantage, leading to a more destabilized metal-centered HOMO as can be seen by the oxidation potentials of the chromium complexes (Table III).

The generally stronger destabilization of the HOMO in the Cr(CO)₄ complexes relative to the molybdenum and tungsten

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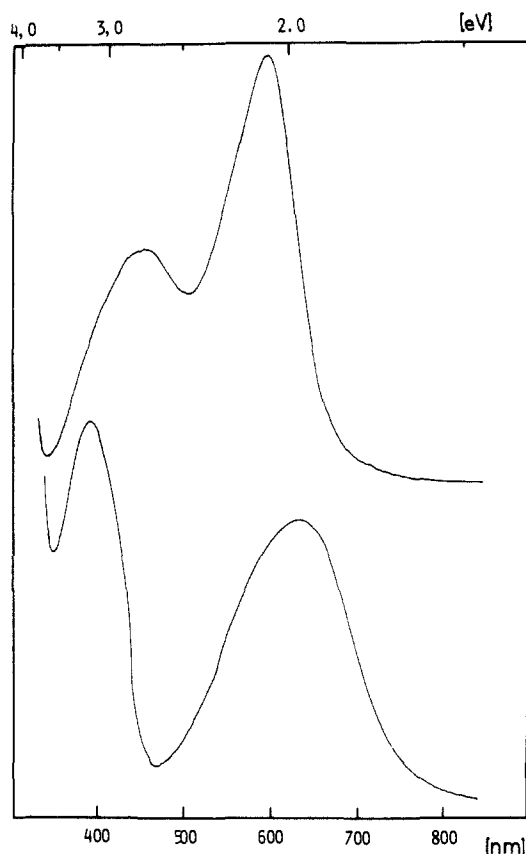(40) Kaim, W.; Ernst, S. *J. Phys. Chem.*, in press.

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Figure 4. Electronic absorption spectra of (bpdz)Mo(CO)₄ (upper spectrum) and (bpm)Mo(CO)₄ (lower spectrum) in toluene solution. The absorbance scale is different for each spectrum.

analogues is also responsible for the fact that the chromium systems display the lowest and the molybdenum species the highest MLCT transition energies throughout the (α-diimine)tetracarbonylmetal series. When comparing these MLCT energies with the differences between oxidation and reduction potentials, e.g., in the chromium complexes, there is a difference of about 0.3 eV (eq 6), which comprises contributions to the Franck–Condon energy from intra- and intermolecular vibrations in the medium.[42] With $\chi \simeq 0.3$ eV, this value is a little larger here than for tris-(α-diimine)ruthenium(II) complexes where $\chi \simeq 0.2$ eV.[49]

$$E_{op}\ [\mathrm{eV}] = \Delta E_{ox/red}\ [\mathrm{V}] + \chi \tag{6}$$

The second major band in the absorption spectra of (bidiazine)tetracarbonylmetal complexes is also due to a symmetry-allowed MLCT transition,[9b] this time, however, from filled metal d levels to the SLUMO of the ligand ($\pi_2{}^* \leftarrow d_{x^2-z^2}$).[44] The justification for such an assignment is not only derived from the absorbance and from the solvatochromic behavior but also from the successful correlation between the experimental differences $\Delta = E_{CT(2)} - E_{CT(1)}$ and the calculated LUMO/SLUMO separations (Figure 1). The averaged values $\Delta = 0.77$ (bpdz), 1.30 (bpm), 1.01 (bpz), and 0.85 eV (bpym) are in agreement with the notion (section 1) that bpdz systems should have the smallest and bpm systems the largest LUMO/SLUMO gap. Figure 4 illustrates both of these extremes for the Mo(CO)₄ complexes.

Remarkably, the different intensity ratios of the two MLCT absorption bands in tetracarbonylmetal complexes of the bidiazines (Table IV, Figure 4) are also related to the π MO calculation results obtained for the ligands (section 3): The two systems (bpdz, bpz) with large LUMO coefficients $c_N{}^2$ at the coordinating centers have $\epsilon_{CT(1)} > \epsilon_{CT(2)}$, whereas the other two ligands (bpm, bpym) with small coefficients $c_N{}^2$(LUMO) form tetracarbonylmetal complexes with $\epsilon_{CT(1)} < \epsilon_{CT(2)}$! Even the average (Cr, Mo, and
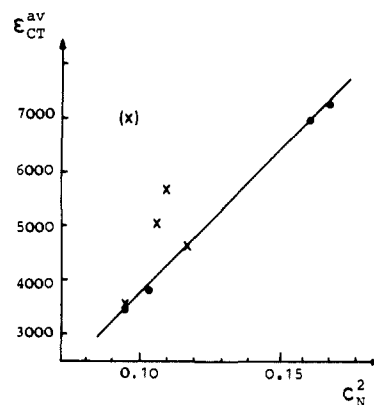

Figure 5. Correlation of averaged (Cr, Mo, and W) extinction coefficients $\epsilon_{CT(1,2)}{}^{av}$ [M⁻¹ cm⁻¹] of MLCT bands in tetracarbonylmetal complexes from Table IV vs. calculated values $c_N{}^2$ for the LUMOs (●) and SLUMOs (×) of the bidiazines (cf. section 3; N refers to the α-diimine nitrogen centers).

W) absolute values of ϵ_{CT} follow the order of HMO coefficients $c_N{}^2$ as illustrated by the good correlation in Figure 5.

Least-squares fit analysis yields $\epsilon_{CT(1)} = -1570 + 5.21 \times 10^4 c_N{}^2$(LUMO) with a correlation coefficient $r = 0.9996$; inclusion of the second charge-transfer absorption bands yields $\epsilon_{CT(1,2)} = -560 + 4.66 \times 10^4 c_N{}^2$(LUMO,SLUMO) with $r = 0.926$. Presumably, some of the $\epsilon_{CT(2)}$ values are too large because of additional contributions from LF or IL (intraligand) transitions; the high value for $\epsilon_{CT(2)}$ in bpym complexes is a result of the near degeneracy of the orbitals b_{3g} and a_u (D_{2h}) in that system (section 3).

The reason for the good correlation in Figure 5 lies in the fact that the transition probability depends on the square of integral (7); all other parameters such as composition, coordination ge-

$$\int_V \psi_n\ \mathbf{r}\ \psi_m\ dV \tag{7}$$

ometry, and MO nodal properties (Chart II) remaining virtually constant, the LUMO wave function is largely responsible for the relative band intensities.

The absorption spectra of the (bidiazine)pentacarbonyltungsten complexes have a different appearance (Figure 5): The solvent-dependent, though less-intense MLCT transitions are found at relatively high energies because the metal-centered HOMO of an M(CO)₅ group is considerably stabilized relative to that of an M(CO)₄ fragment. In agreement with the calculations (section 1), the (bpm)pentacarbonyltungsten complexes absorb at longer wavelengths than the corresponding bpdz analogue; the latter display absorption features similar to those of (4,4′-bipyridine)-pentacarbonyltungsten species.[31] Characteristic for all the W-(CO)₅ complexes is a solvent-independent, relatively narrow absorption band at 3.10 eV = 25 000 cm⁻¹ which may be identified as a ligand-field (LF) transition (¹E ← ¹A).[31,50,51] Figure 6 shows the spectral features discussed by example of the three species observed in reaction sequence (4).

9. Summary. The unique situation for the series in Chart I of isomeric bidiazine ligands with virtually identical coordination geometries and MO nodal properties allows to correlate redox potentials, electronic transition energies, absorption band intensities, and even lifetimes of MLCT excited states of d⁶ metal complexes with the results of straightforward MO perturbation calculations on the ligand π systems. Combined with the experimental data presented in this study, these results serve to delineate the characteristics of each of the bidiazine chelate ligands and suggest their uses for specific purposes in coordination chemistry.

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Characteristics of α-Diimine Ligands

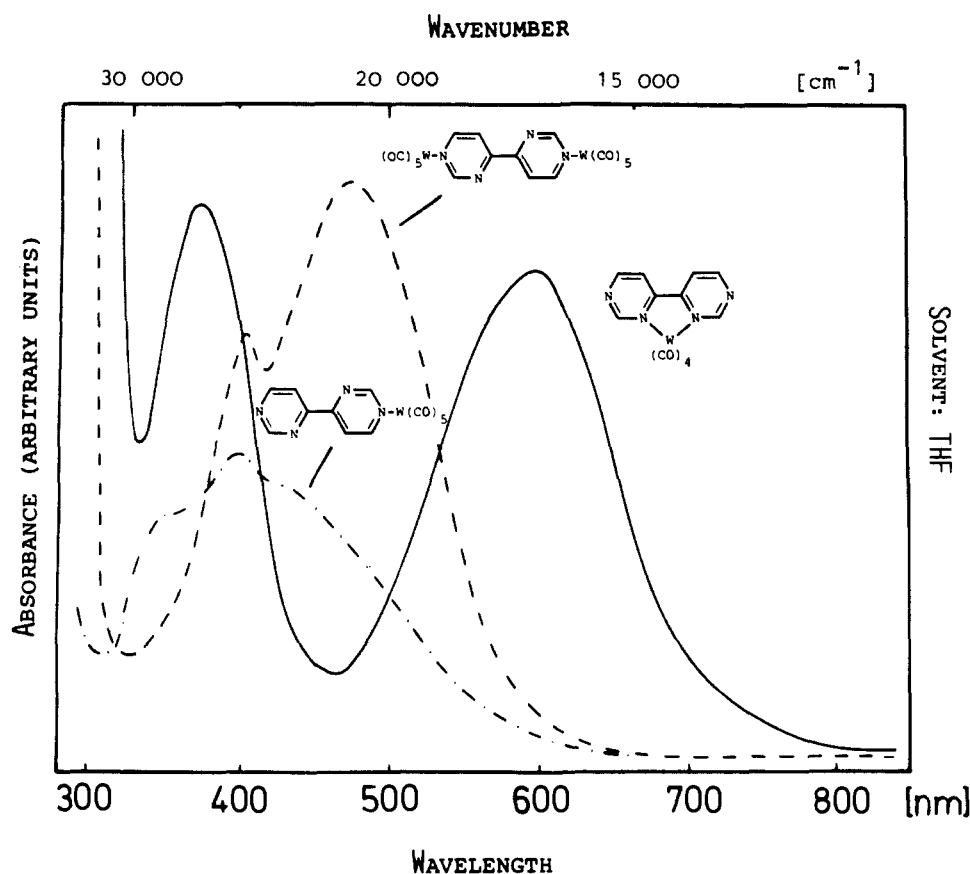*J. Am. Chem. Soc., Vol. 108, No. 13, 1986* 3585

Figure 6. Electronic absorption spectra of the three complexes isolable from reaction sequence (4). The absorbance scale is different for each spectrum.

Bpdz. This ligand exhibits the cloest resemblance to 2,2'-bipyridine, bpy, in having the highest pK_a among all four bidiazines; at the same time, however, its ligand π^* level is considerably lowered relative to that of bpy. The favorable back-bonding situation thus created for metal carbonyl complexes is illustrated, for example, by the dissociative stability of the tetracarbonyl-chromium derivative and by the fact that the first long-wavelength MLCT absorptions occur at lower energies than in corresponding bpz isomers. In agreement with the calculations which predict a rather small LUMO/SLUMO gap for bpdz, the second MLCT absorptions are rather close to the first ones and may still be found in the visible region for $M(CO)_4$ complexes. The calculations further suggest that bpdz should receive a relatively large increase in basicity upon reduction, a result which may explain the dissociative stability and rather long lifetime of the MLCT excited state of $[Ru(bpdz)_3]^{2+}$.

Bpm. As in the case of bpdz, bulky monofunctional fragments $M(CO)_5$ first coordinate to the peripheral nitrogen centers of the ligand before conversion occurs to the thermodynamically more stable $M(CO)_4$ chelate complexes. The most important feature of bpm is its very low-lying π^*-acceptor level due to the nitrogen atom arrangement in the 4,4'-positions of the "biphenyl" 12-center, π-electron system; the ligand is by far the most easily reduced bidiazine without being the weakest base. Accordingly, the first MLCT absorption energies of bpm complexes are the lowest within the bidiazine series, whereas the second MLCT transitions are at very much higher energies since the bpm system is calculated to have a very large LUMO/SLUMO gap.

Bpz. As Crutchley and Lever pointed out, bpz is not a very much better π acceptor than bpy despite its lower lying π^* level; weak σ bonding because of the poorest basicity within the bidiazine series diminishes back-bonding interaction. However, our calculations suggest that the nitrogen centers in reduced bpz receive a very large increase in basicity which explains the good photosensitizing properties of $[Ru(bpz)_3]^{2+}$ (long lifetime of the MLCT excited state)[9a] and the strong response of the excited species on protonation or other additional coordination at the peripheral nitrogen centers.[9]

Bpym. Mononuclear bpym complexes do not exhibit any outstanding features within the bidiazine series; MLCT absorption energies are rather high. However, the ability of the bidiazine chelate ligands to act as bridging ligands, too, makes bpym especially attractive because two chelate-bonded metal centers can be held together at a rather close distance of about 50 pm.[52] Questions concerning medium- and long-range metal–metal interactions have, therefore, instigated several recent studies on the use of this[8,52] and related new binucleating chelate ligands.[33]

A cursory view into the literature shows that ligands of the bpy family are ubiquitous in inorganic and orgametallic coordination chemistry. In some instances, the primary reason to use these ligands is their bidentate nature; in other cases, it is their π-acceptor function. Most frequently, the specific combination of both of these effects is crucial for the successful application of such ligands. Using the set of four isomeric bidiazines with their distinctly different ligand characteristics as outlined in this work, it will now be possible to make clear assessments of the relative significance of σ coordination and π back-donation in α-diimine complexes of specific metal fragments, thus stimulating the synthesis of new kinds of such coordination compounds.

As concerns the methodical approach demonstrated in this study, the effective and comprehensive use of MO perturbation calculations and the successful correlation of the results with a surprising number of physical properties (redox potentials, energies, solvent sensitivity,[48] and absorbance of charge-transfer transitions, lifetimes of MLCT excited states, and ESR coupling constants[40]) can be employed as a general fruitful method for rapid computational screening of many other potentially interesting ligands. We are currently extending our studies both to the bidiazine coordination chemistry of other metal fragments and to further comprehensive ligand screening.

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On the Role of d Orbitals in SF₆

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Abstract: The role of d orbitals in the bonding of SF₆ is studied through natural population and natural hybrid orbital analysis of ab initio SCF wave functions. The sulfur d orbitals are found to contribute very strongly to the binding energy (250 kcal/mol) and to have a total occupancy of around 0.25e, the valence electron distribution on sulfur being about 32% in 3s, 59% in 3p, 8% in 3d, and 1% in 4p. The occupancy of the two sulfur 3d$_\sigma$ orbitals (0.16e), however, is only one-sixth of what would be required for sp³d² hybridization, and the energetic contribution of these orbitals is only two to three times larger than that of the sulfur 3d$_\pi$ orbitals. The sulfur d orbitals are important because they allow strong back transfer from the negatively charged fluorine ligands to the strongly positively charged (+2.9e) sulfur, in turn allowing significant contraction of the S–F bonds and greatly increased molecular stability. Application of the method of natural localized molecular orbitals reveals that the σ_{SF} "bonds" have only one-quarter contribution from sulfur orbitals. The results of this study lead to a refined picture of the nature of hypervalency which is in essential agreement with previous discussions given by Rundle, Musher, and Kutzelnigg, among others. Models of SF₆ requiring sp³d² hybridization should be discarded.

I. Introduction

The Lewis–Langmuir octet theory[1,2] and the concept of valence-shell orbital hybridization[3] have been of great value in understanding the nature of the chemical bonding in compounds of elements of the first row such as acetylene, ethylene, and methane. Extending these ideas to the "hypervalent"[4] compounds of the second and higher row non-metals such as PCl₅, SF₆, I₃⁻, SeCl₄, NSF₃, and XeF₂, however, requires the postulate of a "second valence shell" or "expanded octet",[5,6] and hydridization schemes involving d orbitals[3,7] are invoked for these species.[7-10] Though such a d-orbital hybridization picture has long been criticized on the basis of the large promotion energies involved, the sp³d and sp³d² models are still employed by many chemists.[11,12]

Pauling[3] introduced hybridization involving d orbitals to describe the bonding in transition-metal complexes but judged that, in non-metallic hypervalent species, ionic resonance forms would be much more important than forms involving sp³d and sp³d² hybrids.[13] Many workers, particularly Pimentel,[14] Rundle,[15] Pitzer,[16]

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(9) See, e.g.: Gillespie, R. J. J. Chem. Soc. (London) 1952, 1002–1013. Cilento, G. Chem. Rev. 1960, 60, 147–167. Craig, D. P.; Zauli, C. J. Chem. Phys. 1962, 37, 601–608, 609–615. Cruikshank, D. W. J.; Webster, B. C.; Mayers, D. F. J. Chem. Phys. 1964, 40, 3733–3734.

(10) (a) Mitchell, K. A. R. Chem. Rev. 1969, 69, 157–178. (b) According to Mitchell's eq 6, r_{max} = 3/ζ measures the size of the 3d orbital (in au). We find ζ_{opt} ≃ 2.0 (see Section II), suggesting that 3d has its maximum overlap in the S–F bonding region. On this topic of 3d orbital diffuseness, see also: Coulson, C. A. Nature (London) 1969, 221, 1106–1110.

(11) See, e.g.: (a) Cartmell, E.; Fowles, G. W. A. Valency and Molecular Structure, 4th ed.; Butterworths: London, 1977. (b) Huheey, J. E. Inorganic Chemistry, 2nd ed.; Harper & Row: New York, 1978. (c) Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 4th ed.; John Wiley & Sons: New York, 1980. (d) Hout, R. F.; Pietro, W. J.; Hehre, W. J. A Pictorial Approach to Molecular Structure and Reactivity, John Wiley & Sons: New York, 1984; pp 276–277. (e) Works (a), (b), and (d) favor sp³d and sp³d² models. Work (c) is somewhat critical of these models in Chapter 5 but seems to endorse them on p 504. Huheey writes (p 718), "The question of d orbital participation in nonmetals is still an open controversy.... Inorganic chemists of a more theoretical bent tend to be more skeptical, feeling that the arguments regarding promotion energies and poor overlap have not been adequately solved. On the other hand, chemists interested in synthesis and characterization tend to favor the use of d orbitals in describing these compounds, pointing to the great heuristic value that has been provided by such descriptions in the past and feeling that until rigorous ab initio calculations (not likely in the near future) on these molecules show the absence of significant d orbital participation it is too soon to abandon a useful model."

(12) Maclagan, R. G. A. R. J. Chem. Educ. 1980, 57, 428–429. Critical of the sp³d³ model for SF₆, it points out the fact that this model is taught in most elementary valence courses. Note that Pauling does not mention SF₆ in ref 3, contrary to Maclagan's assertion, and furthermore that his remarks regarding the importance of ionic resonance structures in SF₆ are consistent with Pauling's remarks concerning PCl₅ and PF₅ in ref 13 and in his general chemistry textbooks.

(13) Pauling, L. The Nature of the Chemical Bond, 2nd. ed.; Cornell: Ithaca, 1940; pp 92–93. See also the 3rd. ed.; Cornell, Ithaca, 1960; pp 145–146, 177–178.

(14) Pimentel, G. C. J. Chem. Phys. 1951, 19, 446–448.

(15) (a) Rundle, R. E. Rec. Chem. Progr. 1962, 23, 195–221. (b) Rundle, R. E. Survey Progr. Chem. 1963, 1, 81–130.

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