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The Nature of Reduced and Excited States of π-Electron-Deficient Complexes between $Re(CO)_3Hal$ and Diimine Ligands

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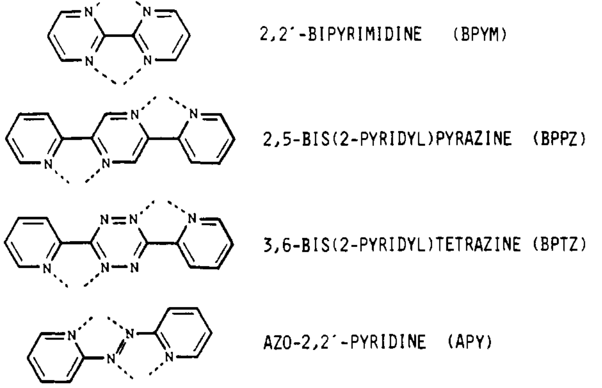
Neutral dinuclear complexes $(\mu\text{-L})[Re(CO)_3Hal]_2$ (Hal = Cl, Br) with the bridging bis-chelate ligands 2,2′-bipyrimidine, 2,5-bis(2-pyridyl)pyrazine, 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, and 2,2′-azopyridine were synthesized. Coordination of two $Re(CO)_3Hal$ fragments causes a very pronounced lowering of the ligand π^* LUMOs, the dinuclear 2,2′-azopyridine complexes being reduced most easily at about +0.45 V vs SCE. The resulting anion-radical complexes were characterized by ESR and, in part, by their visible absorption and carbonyl vibrational spectra. ESR data rule out a "Re(0)" or "Re(0)/Re(I)" formulation for the singly reduced monomers and dimers and show the spectral effect of halide loss for the labile mononuclear complex $(bpy^{\bullet-})Re(CO)_3Br$. The well-separated long wavelength absorption bands from MLCT transitions of the most π-electron-deficient neutral complexes display a distinct structure. A comparison is made between the electronic structures of α-diimine complexes with $W(CO)_4$, $Re(CO)_3Hal$, and $[Ru(bpy)_2]^{2+}$ fragments.

The rather intriguing photo- and electrocatalytic properties of stable complexes such as $(bpy)Re(CO)_3Hal$ (bpy = 2,2′-bipyridine; Hal = Cl, Br)[1-4] have recently given rise to several studies where other, nonconventional α-diimine ligands were employed.[5-8] Emission studies e.g. for the four isomeric bidiazine systems,[8,9] excited state Raman spectroscopy,[10] and ESR data for singly reduced forms[5] revealed a pattern reminiscent of that observed for ruthenium(II) analogues, yet there are clearly differences with respect to the chemical behavior: Both the carbonyl *and* the halide ligands on the rhenium(I) center can be substitutionally labilized photo- and electrochemically.[1-4,11,12]

Employing four symmetrically bis-chelating α-diimine systems (**1**) with very well-established ligand characteristics,[13] we now describe the synthesis and the spectroscopic properties of the dimers (**2**). The bpym dimers had been reported earlier;[7a] we now present the ESR properties of the singly reduced forms[5] as well as an ESR illustration of the catalytically relevant loss of halide in the mononuclear system $(bpy^{\bullet-})Re(CO)_3Br$. Since all new dimeric complexes display well-separated absorption maxima at rather long wavelengths, we could not measure any luminescence;[6,8,14] on the other hand, the facile reducibility of some systems allowed a convenient study of anion-radical complexes[5,15,16] (catalytically active "Re(0)"[1,6,14]) derived from the neutral systems.



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$(\mu\text{-bpym})[Re(CO)_3Hal]_2$ $(\mu\text{-bppz})[Re(CO)_3Cl]_2$

$(\mu\text{-bptz})[Re(CO)_3Hal]_2$ $(\mu\text{-apy})[Re(CO)_3Hal]_2$

Hal = Cl, Br

2

Experimental Section

Instrumentation and Spectra Analysis. ^1H NMR: Bruker WH 270 instrument; solvent as internal standard. ESR: Varian E9 instrument in the X-band; perylene anion radical[17] as reference for a and g (double-cavity technique). Spectra were analyzed by the help of computer simulation[5] with an available program.[18] Initial reproduction of the spectra was performed by using only $^{185,187}Re$ coupling ($I = {}^5/_2$) and Gaussian line shape in order to account for unresolved ligand hyperfine coupling. A first estimate of the $^{185,187}Re$ hyperfine splitting could also be obtained by subtracting established[15] ligand hyperfine coupling (^1H, ^{14}N) from the total spectral width of the chloride systems. In a second stage, different magnitudes of halide coupling ($I = {}^3/_2$) were introduced in order to reproduce the differences in line shape between chloride- and bromide-substituted systems.[5] Directly measured coupling constants are

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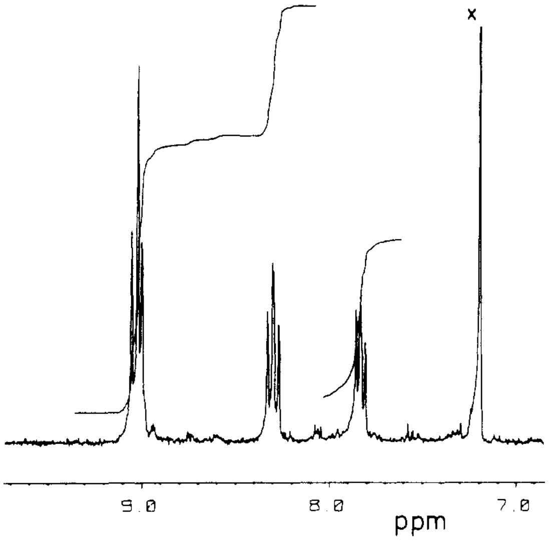


Figure 1. ^{1}H NMR spectrum (low-field section) of (apy)[Re(CO)$_3$Cl]$_2$ in CDCl$_3$ (× denotes CHCl$_3$).

assumed to be correct within ±0.05 mT.[5] IR: Jasco A100 instrument; assumed error ±5 cm^{-1}. UV/vis/near-IR: Shimadzu UV160 instrument; assumed uncertainty ±3 nm. Cyclic voltammetry: potentiostat Model 363 (PAR); function generator Model VSG72 (Bank-Wenking); three-electrode configuration with glassy-carbon working electrode and aqueous SCE reference (liquid junction potential ≈0.15 V); standard scan rate 100 mV/s; assumed relative error ±0.05 V.

Materials. Ligands,[13] pentacarbonylrhenium chloride and bromide,[19] and the known complexes (bpy)Re(CO)$_3$Br[3] and (bpym)[Re(CO)$_3$Hal]$_2$[7] were obtained according to described procedures.

(bppz)[Re(CO)$_3$Cl]$_2$. A 150-mg (0.63-mmol) sample of bppz and 506 mg (1.4 mmol) of Re(CO)$_3$Cl were heated in 100 mL of toluene to 110 °C. The solution turned orange and finally red; after 3 h, there was no more carbonyl evolution. The dark red solid formed on cooling was recrystallized from acetone/hexane to yield 414 mg (78%). Anal. Calcd for $C_{20}H_{10}Cl_2N_4O_6Re_2$ (M_r = 845.63): C, 28.41; H, 1.19; N, 6.63. Found: C, 28.15; H, 1.36; N, 6.39.

(bptz)[Re(CO)$_3$Hal]$_2$ (Hal = Cl, Br). A 150-mg (0.63-mmol) sample of bptz and 1.4 mmol of Re(CO)$_5$Cl (506 mg) or Re(CO)$_5$Br (570 mg) were heated to reflux for 4 h in 100 mL of a mixture containing toluene and dichloromethane (3:1, v/v) until gas evolution ceased. The solvent was removed from the blue solution and the solid residue recrystallized from acetone/hexane to yield 75% of analytically pure complex. Anal. Calcd for $C_{18}H_8Cl_2N_6O_6Re_2$ (M_r = 847.60): C, 25.51; H, 0.95; N, 9.91. Found: C, 25.70; H, 1.12; N, 9.93. Anal. Calcd for $C_{18}H_8Br_2N_6O_6Re_2$ (M_r = 936.50): C, 23.09; H, 0.86; N, 8.97. Found: 23.02; H, 0.98; N, 8.76.

(apy)[Re(CO)$_3$Hal]$_2$ (Hal = Cl, Br). A 150-mg (0.81-mmol) sample of apy and 1.7 mmol of Re(CO)$_5$Cl (615 mg) or Re(CO)$_5$Br (695 mg) were heated to reflux for 4 h in 100 mL of a mixture containing toluene and dichloromethane (3:1, v/v) until gas evolution ceased. The color changed from purple (mononuclear complexes) to blue green. The solvent was removed from the solution and the solid residue recrystallized from acetone/hexane to yield 80% of dark green complex. Anal. Calcd for $C_{16}H_8Cl_2N_4O_6Re_2$ (M_r = 795.74): C, 24.16; H, 1.01; N, 7.05. Found: C, 24.36; H, 1.24; N, 7.22. Anal. Calcd for $C_{16}H_8Br_2N_4O_6Re_2$ (M_r = 884.47): C, 21.73; H, 0.91; N, 6.33. Found: 22.44; H, 1.21; N, 6.62.

(apy)[Re(CO)$_3$Cl]$_2$ and (bptz)[Re(CO)$_3$Cl]$_2$ were reduced quantitatively for IR and UV/vis spectroscopic purposes by using cobaltocene as reductant.[20] Anion-radical complexes for ESR measurements were obtained by *intra muros* electrolysis in a two-electrode cell.[9b]

Results

The complexes (**2**) were prepared from the free ligands (**1**) and the (CO)$_5$ReHal precursors via thermal substitution reactions (1).

$$\mu\text{-L} + 2(\text{CO})_5\text{ReHal} \xrightarrow{\Delta} (\mu\text{-L})[\text{Re(CO)}_3\text{Hal}]_2 + 4\text{CO} \qquad (1)$$

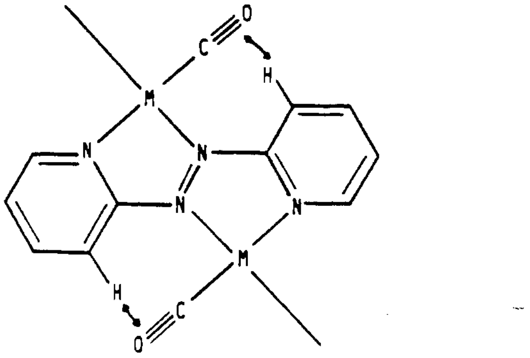
Table I. Carbonyl Vibrational Frequencies ν_{CO} (cm^{-1}) in THF Solution and Calculated Force Constants (mdyn/Å)

	ν_{CO}					
complex	A′	A″	A′	k_1	k_2	k_i
(bpym)[Re(CO)$_3$Cl]$_2$	2025	1938	1900	14.69	15.97	0.47
(bppz)[Re(CO)$_3$Cl]$_2$[a]	2050	1950	1930	14.48	16.66	0.55
(bptz)[Re(CO)$_3$Cl]$_2$	2010	1950	1921	14.96	15.86	0.39
(bptz)[Re(CO)$_3$Br]$_2$	2010	1959	1921	14.96	15.86	0.39
(apy)[Re(CO)$_3$Cl]$_2$	2005	1952	1938	15.01	16.01	0.37
(apy)[Re(CO)$_3$Br]$_2$	2005	1948	1938	14.93	16.07	0.38
(bptz$^{\bullet-}$)[Re(CO)$_3$Cl]$_2$	2015	1918	1898	14.36	16.09	0.49
(apy$^{\bullet-}$)[Re(CO)$_3$Cl]$_2$	2003	1910	1895	14.30	16.02	0.50

[a] In acetone solution.

Three carbonyl stretching bands were observed for each of the products, the two low-energy bands being rather closely spaced. The wave numbers and the force constants calculated according to the Cotton–Kraihanzel method[21] are summarized in Table I.

A 270-MHz ^{1}H-NMR spectrum was taken for an apy dimer (Figure 1) since steric interference between H(3,3′) and equatorial carbonyl groups (**3**) has previously been shown to result in an unusual sequence of chemical shifts for the 2-pyridyl protons.[13] Also, the question of cis/trans isomerism[6] of the halide substituents (**4**) was addressed by that experiment.



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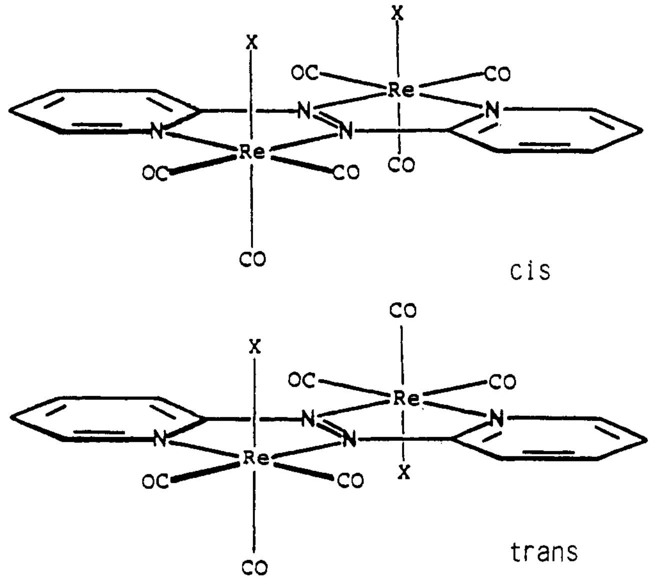

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Cyclic voltammetry in 1,2-dichloroethane or acetonitrile solution revealed reversible one-electron reductions to the respective anion-radical complexes at very positive potentials; the second one-electron-reduction processes proved to be considerably less

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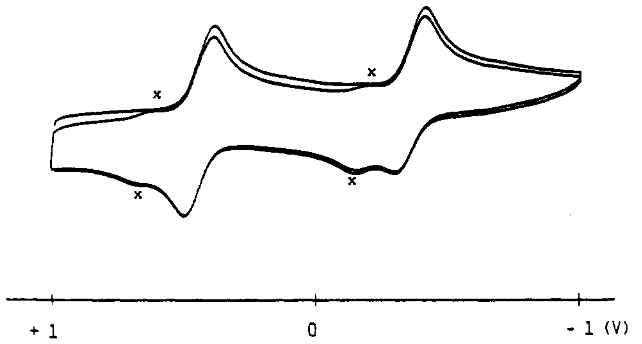


Figure 2. Cyclic voltammogram of (apy)[Re(CO)$_3$Cl]$_2$ in 1,2-dichloroethane/0.1 M tetrabutylammonium perchlorate. × denotes the signals of (dehalogenated) decomposition product(s) formed only after the second reduction.

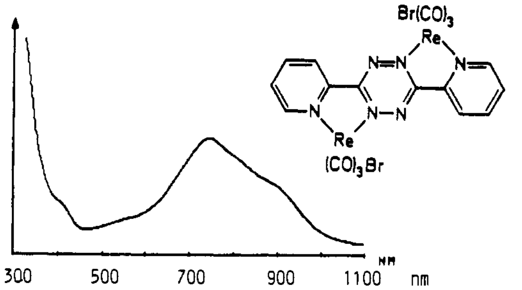


Figure 3. Absorption spectrum of (bptz)[Re(CO)$_3$Br]$_2$ in 1,2-dichloroethane.

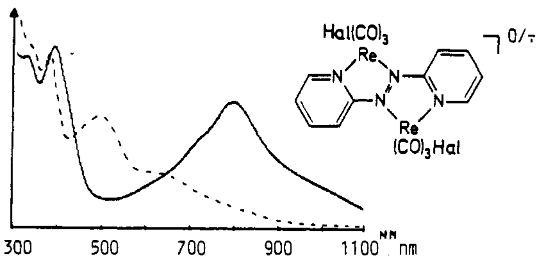


Figure 4. Absorption spectra of (apy)[Re(CO)$_3$Br]$_2$ (—) and {(apy)[Re(CO)$_3$Cl]$_2$}$^{\bullet-}$ (- -) in 1,2-dichloroethane (absorbance scale different for each spectrum).

Table II. Reduction Potentials E_{red} (V vs SCE) of Ligands and Dinuclear *fac*-Tricarbonylrhenium(I) Halide Complexes[a]

compound	E_{red_1} (ΔE)[b]	E_{red_2} (ΔE)[b]	solvent
bpym	−1.73	−2.44 (i)	DMF
[Re(CO)$_3$Cl]$_2$(bpym)	−0.34 (60)	−1.02 (100)	AN
[Re(CO)$_3$Cl]$_2$(bpym)[c]	−0.51	−1.20	DMF
bppz	−1.49	−2.2 (i)	DMF
[Re(CO)$_3$Cl]$_2$(bppz)	−0.36 (170)	−1.01 (200)	AN
bptz	−0.72	−2.2 (i)	DMF
[Re(CO)$_3$Cl]$_2$(bptz)	+0.33 (70)	−1.00 (i)	DCE
[Re(CO)$_3$Br]$_2$(bptz)	+0.31 (65)	−0.95 (i)	DCE
apy	−0.96	−1.60 (i)	DMF
[Re(CO)$_3$Cl]$_2$(apy)	+0.45 (70)	−0.35 (80)	DCE
[Re(CO)$_3$Br]$_2$(apy)	+0.44 (80)	−0.35 (90)	DCE

[a] Measurements in 0.1 M solutions of $Bu_4N^+ClO_4^-$; no correction for liquid junction potential (estimated to be about 0.15 V). DCE = 1,2-dichloroethane, AN = acetonitrile, and DMF = *N*,*N*-dimethylformamide. Values for ligands were taken from ref 13. (i) denotes an irreversible process (peak potential given). [b] ΔE is the difference between anodic and cathodic peak potentials in mV. [c] Reference 6.

Table III. Long Wavelength Absorption Maxima λ_{max} (nm) and E_{op} (eV) for Dinuclear Re(I), Mo(0), and W(0) Chelate Complexes

complex	λ_{max}	E_{op}	solvent
(bpym)[Re(CO)$_3$Cl]$_2$	469,[a] 357[b,c]	2.64	Me$_2$CO
(bpym)[Re(CO)$_3$Br]$_2$	472,[a] 364[b,c]	2.62	Me$_2$CO
(bpym)[Mo(CO)$_4$]$_2$	606,[a] 426,[b] 389[c]	2.05	THF
(bppz)[Re(CO)$_3$Cl]$_2$	504,[a] 348[b]	2.46	Me$_2$CO
	519,[a] 357[b]	2.39	DCE
(bppz)[W(CO)$_4$]$_2$	678,[a] 480[b]	1.83	THF
(bptz)[Re(CO)$_3$Cl]$_2$	697,[a] 510 (sh)[b]	1.78	Me$_2$CO
	732,[a] 520 (sh)[b]	1.69	DCE
(bptz)[Re(CO)$_3$Br]$_2$	700,[a] 510 (sh)[b]	1.77	Me$_2$CO
	900 (sh), 736[a] 520 (sh),[b] 410 (sh)[c]	1.68	DCE
(bptz)[W(CO)$_4$]$_2$	855,[a] 540[b]	1.45	THF
(apy)[Re(CO)$_3$Cl]$_2$	761,[a,d] 406[c]	1.63	Me$_2$CO
	779,[a,d] 395[c]	1.59	DCE
(apy)[Re(CO)$_3$Br]$_2$	770,[a,d] 392[c]	1.61	Me$_2$CO
	796[a,d] (ϵ = 6600) 394[c] (ϵ = 8000)	1.56	DCE
(apy)[Mo(CO)$_4$]$_2$	900[a]	1.38	THF
(apy$^{\bullet-}$)[Re(CO)$_3$Cl]$_2$[g]	610,[c] 484,[a,c] 369[c]	2.56	DCE
(apy$^{\bullet-}$)[Re(CO)$_3$Br]$_2$[g]	620,[c] 496,[a,c] 381[c]	2.50	DCE

[a] MLCT I. [b] MLCT II. [c] Non-MLCT band; Cf. text. [d] Structured band; see Figure 4. [e] For the first absorption maximum. [f] Me$_2$CO = acetone; DCE = 1,2-dichloroethane. [g] Counterion CoCp$_2^+$.

Table IV. Isotopic Properties of Coupling Nuclei

isotope	natural abundance, %	nuclear spin	A_{iso},[a] mT
^{1}H	99.98	$^1/_2$	50.8
^{14}N	99.63	1	55.7
^{35}Cl	75.4	$^3/_2$	167.2
^{37}Cl	34.6	$^3/_2$	139.1
^{79}Br	50.6	$^3/_2$	776.4
^{81}Br	49.4	$^3/_2$	837.0
^{185}Re	67.5	$^5/_2$	927.4
^{187}Re	32.5	$^5/_2$	926.9

[a] Isotropic hyperfine coupling constant, from ref 22.

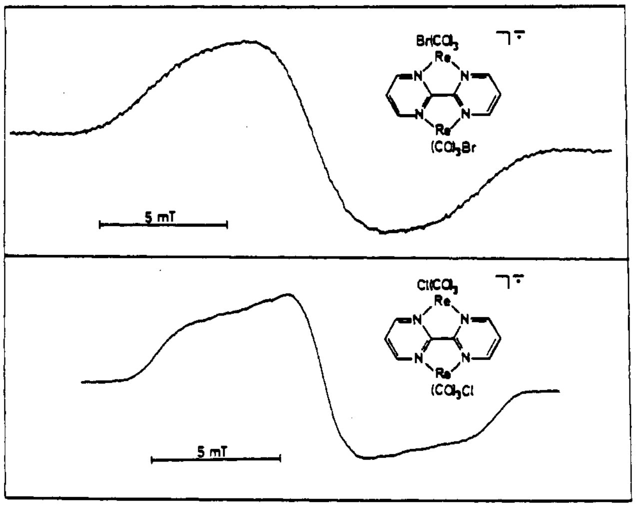


Figure 5. ESR spectra in acetone solution of {(bpym)[Re(CO)$_3$Hal]$_2$}$^{\bullet-}$: (top) Hal = Br; (bottom) Hal = Cl.

reversible[8] as illustrated by Figure 2 and summarized in Table II. Irreversible oxidation processes were observed for all complexes around +1.7 V vs SCE.

Two typical absorption spectra of the neutral dimers in the near-ultraviolet, visible, and near-infrared regions are shown in Figures 3 and 4; the maxima are given in Table III. Figure 4 also illustrates the changes occurring on one-electron reduction.

All compounds could be studied in their singly reduced forms by ESR spectroscopy after electrochemical reduction within an ESR cavity.[5] The magnetic properties of the relevant nuclei are listed in Table IV; representative spectra are shown in Figure 5 and were briefly discussed previously.[5] Figure 6 illustrates the ESR spectroscopic effect of halide loss of the mononuclear complex (bpy$^{\bullet-}$)Re(CO)$_3$Br; Table V summarizes isotropic g factors, spectral widths, and isotope coupling constants as extracted from resolved hyperfine lines or from computer simulations of line shapes.[5]

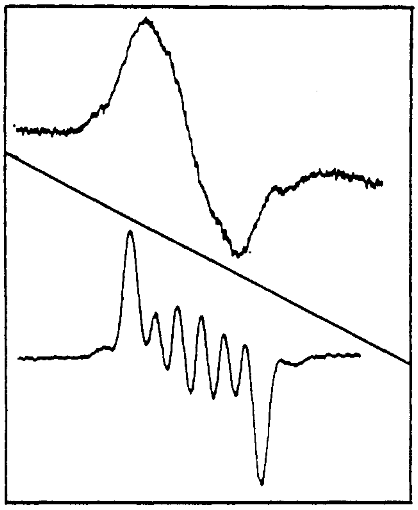


Figure 6. ESR spectra of $[(bpy)Re(CO)_3Br]^{\bullet-}$ in acetone immediately after electrolytic generation (top) and after 15 min (bottom), showing the spectral effect of halide loss.

Table V. ESR Parameters for Re(I) Anion-Radical Complexes

radical complex	g	ΔH^a	$a_{Re}{}^b$	$a_{Hal}{}^b$	solvent^d
$(bpy^{\bullet-})[Re(CO)_3Cl]$	2.0032	11	1.2	(0.2)	Me_2CO
$(bpy^{\bullet-})[Re(CO)_3Br]$	2.0023	14	(1.2)	(1.2^c)	Me_2CO
$(bpy^{\bullet-})[Re^+(CO)_3L]^d$	2.0033	11.6	1.54		Me_2CO
$(bpym^{\bullet-})[Re(CO)_3Cl]_2$	2.0005	16	(1.2)	(0.2)	Me_2CO
$(bpym^{\bullet-})[Re(CO)_3Br]_2$	2.0005	19	(1.2)	(0.8^c)	Me_2CO
$(bptz^{\bullet-})[Re(CO)_3Cl]_2$	2.0051	29	(2.2)	(0.2)	DCE
$(bptz^{\bullet-})[Re(CO)_3Br]_2$	2.0045	31	(2.2)	(0.5^c)	DCE
$(apy^{\bullet-})[Re(CO)_3Cl]_2$	2.0039	35	2.54	(0.2)	DCE
$(apy^{\bullet-})[Re(CO)_3Br]_2$	2.0040	40	(2.54)	(1.0^c)	DCE

^{a}Total spectral width (in mT). ^{b}Coupling constants in mT; for isotope characteristics, see Table IV. Values in brackets were inferred from a computer simulation (±0.2 mT). ^{c}Assuming the same metal coupling as for the chloride. ^{d}Me_2CO = acetone, DCE = 1,2-dichloroethane.

Discussion

Isomerism and Structure. The pattern of carbonyl stretching bands for all neutral and anionic systems investigated suggests the *fac* configuration at the six-coordinated metal centers, in agreement with previous results.[1-8,10-12,23,24] Inequivalence of the non-carbonyl coordination sites leads to a small splitting of the low-energy E band into A″ and A′.[21] The IR carbonyl stretching bands do not allow a straightforward distinction between cis/trans isomers (**4**) for symmetrical dimers; such a distinction should be possible on the basis of high-resolution ^1H NMR studies as has been demonstrated previously for the complex (bpym)[Re(CO)$_3$Cl]$_2$.[6] However, only one isomer could be seen in a 270-MHz spectrum of (apy)[Re(CO)$_3$Cl]$_2$ (Figure 1). This spectrum also illustrates a virtual coincidence of chemical shifts for the protons H(3,3′) and H(6,6′); the rhenium system thus shows about half the effect of the Mo(CO)$_4$ dimer, which displays δ(H(3,3′)) > δ(H(6,6′)), i.e., the opposite effect to the normal situation δ(H(6,6′)) > δ(H(3,3′)) in unperturbed 2-pyridyl rings.[13] This intermediate position of the rhenium complex suggests a slight relief of steric strain because of longer metal–ligand bonds; the still very compact arrangement (**4**) may be responsible for the occurrence of only one isomer,[6] which we tentatively identify as the trans species. The effects of such isomerism on the electronic structure should be very small.[6]

Electronic Structure as a Function of the Bridging Ligand. Previous studies have shown that the energy of the ligand-based LUMO decreases in the order bpym > bppz ≫ bptz > apy for dinuclear complexes.[9a,13] The latter relation is different from the relation $E(\pi^*)$:apy > $E(\pi^*)$:bptz found for the *free* ligands;[13] this is a result of stronger response toward coordination of electrophiles by the apy system in which two-thirds of the total LUMO π-electron "population" is concentrated at the coordinating nitrogen centers ($\sum c_N{}^2 = 0.664$ as compared to $\sum c_N{}^2 = 0.500$ for bptz).[13]

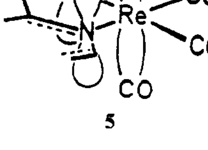
The Cotton/Kraihanzel analysis[21] of the carbonyl vibrational frequencies confirms this sequence; the smallest interaction constants k_i, indicating the ligand most similar to carbonyl π-acceptor groups,[13,21] are found for the apy and bptz dimers. Larger values were calculated for complexes of the weaker π acceptors bpym and bppz as well as for *reduced* apy and bptz complexes; it is not surprising that single occupation of the π^* level reduces the π-acceptor capability of such an unsaturated ligand. It is also noteworthy that the smallest values k_1 and k_2 were calculated for the anion-radical systems; anion radicals, especially those with large $c_N{}^2$ values, are quite basic ligands.[15a]

Reducibility and Reactivity. Reduction potentials of the complexes (Table II) also illustrate the aforementioned sequence of bridging ligands; on the other hand, the effect of the halide exchange Cl/Br is very small. The absolute values show a remarkable shift of reduction potentials through metal coordination; it should be noted here that the effect of neutral Re(CO)$_3$Hal fragments exceeds that of most other metal fragments including Mo(CO)$_4$,[13] $[Ru(bpy)_2]^{2+}$,[9] $[Os(bpy)_2]^{2+}$,[25] [Rh(norbornadiene)]$^+$,[26] PtPh$_2$,[27] and $[Cu(PR_3)_2]^+$.[28] The apy dimers are thus easier to reduce than even TCNE or TCNQ[29] by about 0.2 V; however, the presence of halide ligands diminishes the reversibility of reduction[8] even at rather positive potentials. Figure 2 illustrates that the formation of a dianionic ligand (fully occupied π^* orbital) results in the appearance of new signals in the cyclovoltammogram; the loss of halide ions to regain neutrality and the substitution by solvent molecules or other substrates such as phosphanes[12,30] is an obvious reaction. Such effects are less pronounced if the two unsaturated N coordination sites are virtually decoupled as in the doubly reduced form of [Re(CO)$_3$Cl(4-bzpy)$_2$] (4-bzpy = 4-benzoylpyridine).[16]

The peak potential differences between the first and second reductions are typical for each ligand system,[9,13] confirming the ligand character of the LUMO; similarly, total irreversibility of the second reduction step has frequently been observed for 1,2,4,5-tetrazines.[9,13,31]

Oxidation occurs at rather positive potentials around +1.7 V vs SCE. The irreversibility is compatible with the predominant metal d character of the orbital involved; formation of rhenium(II) may lead to the loss of carbonyl ligands[6,8] and to eventual formation of halogens at such high potentials.

The different kinds of substitutional lability of axial ligands (**5**) on reduction (halide activation) and oxidation (CO activation) are quite important in designing electrocatalytic rhenium(I) complexes and their solvation environment;[1,2,12] a similar ambivalent behavior of such compounds has been observed in their photochemistry.[11]



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ESR of the Reduced State. Proof for the anion-radical character of the singly reduced forms and evidence against their designation as "Re(0)"[1,6,14b] (or even as mixed-valent "Re(0)/Re(I)" for the dimers) comes from ESR spectroscopy of these species.[5] The monoanions show strong ESR signals at room temperature that might not always be expected in a mixed-valence dimer situation involving heavy-metal centers.[26,32] The spectra are rather broad and much less well resolved (Figures 5 and 6) than those of the $M(CO)_4$ analogues (M = Cr, Mo, W).[15b,c] The reason lies in the small unresolved coupling from the halide nuclei which are situated in a favourable (axial) conformation for σ/π hyperconjugation.[15b,33] Overlap of this splitting with the ^1H and ^{14}N hyperfine coupling from the heterocycles[15b,c] and with the 11 lines (intensity ratio of 1:2:3:4:5:6:5:4:3:2:1) resulting from interaction with two equivalent $^{185,187}Re$ nuclei[5] necessarily produces spectra with little total resolution; some additional broading due to the large spin-orbit coupling constant of rhenium[22] and insufficient averaging of anisotropic contributions (g, a_{Re}) also have to be considered.[15c,22]

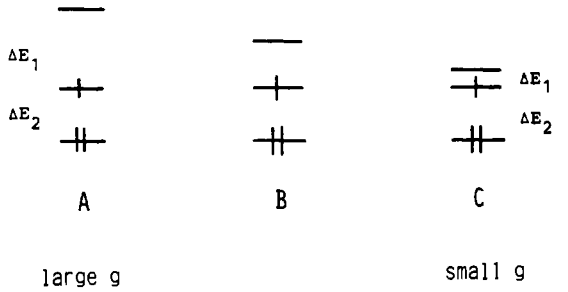
The rhenium coupling constants (Table V) as measured directly from a few sufficiently resolved examples[5] and as estimated via spectral widths and computer simulations[5] clearly indicate the anion-radical nature of the paramagnetic complexes. In comparison to the isotropic hyperfine coupling constant A_{iso} of about 927 mT for these isotopes (Table IV) the observed coupling constants amount to far less than 1%. The differences in magnitude for $a(^{185,187}Re)$ reflect the established spin densities at the coordinating nitrogen centers of these anion-radical ligands;[15b,c] the largest value is measured for the apy system. Halide exchange from chloride to bromide, although virtually without effect on the reduction potentials, changes the appearance of the ESR spectra quite distinctly;[5] it is well established that coupling from $^{79,81}Br$ is about 5 times as large as coupling from $^{35,37}Cl$ nuclei in a comparable environment.[34] The broadening effect of bromine is thus larger than that of chlorine atoms as reflected, e.g., in the line shapes of the bpym dimers (Figure 5). The chloride still shows a characteristic signal form[5] whereas homogeneous line broadening due to increased overlap in the bromide produces a featureless, almost Gaussian line shape.

A similar broadening effect may be noted when comparing the reported spectrum[5] of the mononuclear $(bpy^{\bullet-})Re(CO)_3Cl$ with that of the bromide analogue (Figure 6); ultimate substitution of the halide in the molecular anion by the solvent (eq 2) produces

$$[(bpy^{\bullet-})Re(CO)_3Br]^{\bullet-} \xrightarrow{\text{solvent S}} [(bpy^{\bullet-})Re(CO)_3(S)]^{\bullet} + Br^- \qquad (2)$$

a sextet spectrum that shows much better resolution than that of either the bromide or the chloride. An additional reason for this improved resolution is a slight increase of the metal coupling constant after removal of the spin-delocalizing halide nucleus (Table V). Spin transfer to axial ligands in situation **5** is not uncommon and has been observed most often for phosphane ligands;[15a,b,33,35] our interpretation has been to invoke low-lying σ^* (M–X) orbitals interacting with the spin-bearing π system.[33] (Formula **5** depicts the bonding σ orbital.)

Whereas the heavy rhenium centers cause a pronounced line broadening in conjunction with the halide ligands, the isotropic g values of the radical complexes are only marginally affected by these metal centers with their large spin–orbit coupling constant of about 2000 cm^{-1}.[22] This result stands in marked contrast to the observations made for corresponding anion-radical complexes with d^6 heavy-metal centers such as $W(CO)_4$ (larger g)[15c] or $[Ru,Os(bpy)_2]^{2+}$ (smaller g).[9b] Typically, the bpym dimers exhibit the smallest isotropic g values;[15b] however, the other complexes have almost the same g-factors as the corresponding free ligands.[15b,c,36] Such an unexpected lack of g shift may be attributed[15] to a molecular orbital situation (**6B**) in which a not too low-lying excited state contributes to the electronic structure of the doublet species. We have noted in the past for complexes of $(C_5R_5)(CO)_2Mn$,[37] $(PR_3)_2(CO)_2Mo$,[33b] and $(bpy)_2Ru^{2+}$ [9b] that small g values of the singly reduced form often correlate with highly photodissociative (d–d) excited states lying close to the lowest MLCT-excited state (**7**). In agreement with the intermediate g of the Re(I) radical complexes, the neutral systems display moderate photoreactivity in terms of CO or halide dissociation.[1,11,14]



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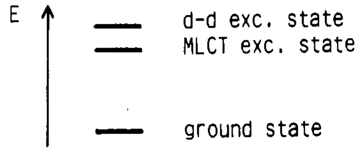

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Absorption Spectra. The very low-lying π^* orbitals of coordinated apy and bptz ligands allow one to observe very well-separated long-wavelength absorption bands for the low-energy MLCT transitions (Figures 3 and 4). The ligand-reduced states discussed before bear some resemblance to the MLCT excited state, be it localized or delocalized with respect to the two chemically equivalent metal centers (eqs 3 and 4).

$$(L)[Re^{I}(CO)_3Hal]_2 \xrightarrow{+e^-} \{(L^{\bullet-})[Re^{I}(CO)_3Hal]_2\}^{\bullet-} \qquad (3)$$

$$(L)[Re^{I}(CO)_3Hal]_2 \xrightarrow{h\nu} {}^*\{(L^{\bullet-})[Re^{1.5}(CO)_3Hal]\} \text{ or } {}^*[Hal(CO)_3Re^{I}(L^{\bullet-})Re^{II}(CO)_3Hal] \qquad (4)$$

There should be at least three transitions possible from the doubly filled d orbitals of the t_{2g} set (**7**), with the two less overlap- and symmetry-favored transitions becoming better resolved in nonpolar solvents.[29b,38] Comparative studies have shown that heavy metal centers with their large spin–orbit coupling constants can cause these overlap-disfavored transitions to become quite intense.[29b,37] Indeed, Figures 3 and 4 show the long-wavelength maxima, each accompanied by high- and low-energy shoulders. The extinction coefficient measured for one apy dimer (Table III) is distinctly *smaller* than the values $\epsilon > 10000$ M^{-1} cm^{-1} observed for corresponding $Mo(CO)_4$[13] or $[(bpy)_2Ru]^{2+}$ systems.[9a]

While the bptz ligand offers a rather low-lying second unoccupied MO (SLUMO) for a fairly weak MLCT transition[13] (Figure 3, Table III), the apy system is characterized by a very large LUMO/SLUMO gap and predictably weak second and third MLCT transitions.[13] However, the rhenium(I) dimers of

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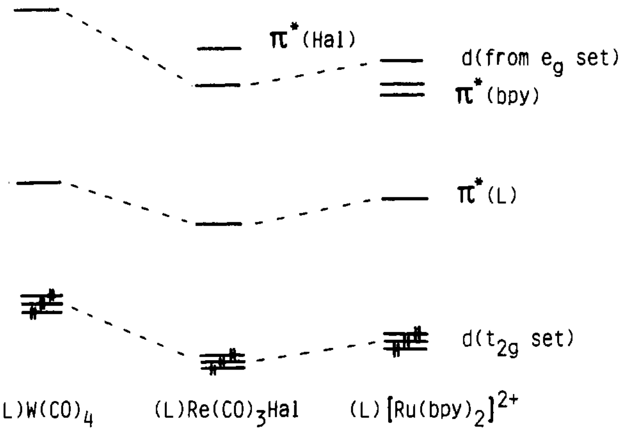
apy show an intense, rather narrow second transition around 400 nm (Figure 4), which cannot be attributed to an MLCT process Re(I) → apy. The excited state connected with this transition may be viewed in connection with the unusually small *g* values of the corresponding anion radicals; there are several observations in the literature pointing to the possibility of charge transfer from heavy-metal centers (Mo, Tc, Re) to halide ligands.[39] An alternative assignment of this band to a (singlet) intraligand transition $\pi \rightarrow \pi^*$ would imply an unprecedented[38b] shift of more than 8000 cm^{-1} with respect to the absorption maximum of the free ligand;[40] on the other hand, the presence of two heavy metal centers with large spin-orbit coupling constants might favor intense d → d triplet absorption features as, e.g., in complexes of osmium.[41]

Although all dimers have rather low-lying π^* orbitals, the absorption maxima of the rhenium systems lie somewhat higher in energy than those of related tungsten or molybdenum tetracarbonyl complexes;[15b,c] this is a consequence of the strongly stabilized filled metal d orbitals as illustrated by very positive oxidation potentials. Considering all informations from electrochemistry, ESR, and electronic absorption spectroscopy, we arrive at comparative representations (**8**) for the frontier orbital situations in complexes of $W(CO)_4$,[13,15b] $Re(CO)_3Hal$, and $[Ru(bpy)_2]^{2+}$[9] with strongly π-accepting α-diimines.



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Reduction of the bpym[42] and apy dimers (Figure 4) yields absorption spectra very similar to those of corresponding ligand anion radicals[40] (Table III); the MLCT transition is reduced in intensity (half-occupied target orbital) and shifted hypsochromically because of additional $d(t_{2g})$ stabilization by the now anionic unsaturated ligand.[15,43]

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Extended Hückel MO Studies of Boranes. 1. Relative Stabilities of *closo*-B_nH_n and -$B_nH_n^{2-}$

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Series of extended Hückel molecular orbital (EHMO) calculations are reported for *closo*-boranes $B_nH_n^{m-}$, where $n = 3-12$ and $m = 0$ or 2. Calculations have been carried out for published experimental geometries and also for hypothetical structures in which (a) all boron atoms lie on a spherical surface, and (b) all polyhedral faces are equilateral triangles with B-B = 1.70 Å, with exo-radial-hydrogen atoms at B-H = 1.19 Å. The manner in which orbital energy levels (classified by using Stone's nomenclature) and total electronic energies vary with *n* are noted and used to explore the pattern of disproportionation of clusters $B_nH_n^{2-}$, and to rationalize the existence and relative stabilities of halides B_nX_n (n = 4, 7-12). The known chemical behavior of anions $B_nH_n^{2-}$ is well reproduced by the calculations using equilateral triangular faced model structures, suggesting that atom connectivities are more important in these systems than other structural features such as relative bond lengths or electronic features such as halogen back-donation.

This is the first of a short series of papers exploring the value of systematic EHMO calculations for understanding, explaining, or predicting aspects of the chemistry and structural preferences of closo, nido, and arachno clusters of the borane type. In the present paper we consider *closo*-borane anions $B_nH_n^{2-}$ and neutral closo halides B_nX_n, and show how their relative stabilities can be rationalized by calculations on model systems with equilateral triangular polyhedron faces, illustrating the importance of atom connectivities and topological influences. In subsequent papers we shall show how EHMO calculations allow the shapes of nido and arachno systems to be rationalized or predicted and draw attention to the importance of endo ligands such as the *m* endo-hydrogen atoms of neutral boranes B_nH_{n+m}, the locations of which can in general be predicted from frontier orbital considerations.

The exclusively triangular-faced polyhedral structures of the borane anions $B_nH_n^{2-}$ (n = 6-12 and neutral halides B_nX_n (n = 4, 7-12) (Figure 1) are familiar features of boron cluster chemistry.[1-6] The topological basis for the prevalence of deltahedral structures has been discussed by a number of authors (see, e.g., refs 7-10 and others cited therein), who have noted that such

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