ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/233038344

The δ in 18 + δ Electron Complexes: Importance of the Metal/Ligand Interface for the Substitutional Reactivity of "Re(0)" Complexes (α-diimine -)Re I (CO) 3 (X)

ARTICLE *in* ORGANOMETALLICS · JANUARY 1996

Impact Factor: 4.13 · DOI: 10.1021/om950500e

CITATIONS
121

READS
28

3 AUTHORS, INCLUDING:

Axel Klein
University of Cologne
185 PUBLICATIONS **2,883** CITATIONS

SEE PROFILE

Available from: Axel Klein
Retrieved on: 16 January 2016

The δ in 18 + δ Electron Complexes: Importance of the Metal/Ligand Interface for the Substitutional Reactivity of "Re(0)" Complexes (α-diimine$^-$)Re^I(CO)$_3$(X)

Axel Klein, Conny Vogler, and Wolfgang Kaim*

Institut für Anorganische Chemie der Universität, D-70550 Stuttgart, Germany

Received June 27, 1995[⊗]

The factors determining the electron transfer-induced halide labilization in complexes (α-diimine)Re(CO)$_3$(Hal), Hal = Cl and Br, were systematically studied via EPR and cyclic voltammetry in the presence of substituting ligands such as triphenylphosphine, cyanide, or acetonitrile. The α-diimines employed were the four isomeric bidiazines (bdz) 3,3′-bipyridazine, 2,2′-bipyrazine, and 2,2′- and 4,4′-bipyrimidine and the nonaromatic α-diimines 1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene (dab) and 1,3-di-*tert*-butylsulfurdiimine (sdi). For comparison, the complexes (L)Re(CO$_3$)Cl, L = 2,2′-bipyridine, 1,4,7,10-tetraazaphenanthrene, and η^2-2,2′,2″-terpyridine, and the new cationic species [(bdz)Re(CO)$_3$(CH$_3$CN)]$^+$ were also investigated. In a further experiment, *in situ* EPR spectroelectrochemistry was employed to study the primary paramagnetic intermediates during the reduction of the prototype compound, (bpy)Re(CO)$_3$Cl, under a CO_2 atmosphere. The susceptibility to substitution was found to be dependent not on the redox potential but on the π molecular orbital coefficients at the metal-coordinating nitrogen centers which are reflected by ^{14}N, ^{185,187}Re, and ^{31}P EPR coupling constants. The most labile systems were thus found among the complexes of the small dab and sdi ligands, despite their facile reduction. In contrast, the complexes of these nonaromatic compounds showed an electrochemically reversible one-electron oxidation which, in comparison to the absorption maximum, allowed us to estimate contributions to the reorganization energy of the MLCT excited state in two cases. For the reductive labilization, it is primarily the small but variable and EPR-detectable ligand-to-metal electron (spin) transfer at the metal/ligand interface which determines the extent of activation in 18 + δ valence electron intermediates.

In previous work we have introduced the term "18 + δ"[1,2] for the valence electron configuration of the metal in paramagnetic carbonyl complexes or related species where the organometallic complex fragment receives a small but EPR-detectable amount of unpaired electron density from coordinated reduced, i.e. anion radical, ligands.[3] We[1] and others[4] could show that this small effect of charge delocalization can result in a selective substitutional activation which may even proceed catalytically[1] (electron transfer catalysis[2a,5]). Furthermore, the compounds which resulted from CO substitution by triorganophosphines are new donor/acceptor substituted metal carbonyl complexes with decreased frontier orbital energy gaps.[1]

In this paper we describe the electron transfer-induced substitution of halide ligands by triphenylphosphine and other donors such as cyanide or acetonitrile in the reduced forms of the complexes (α-diimine)Re(CO)$_3$(Hal), Hal = Cl and Br, where the α-diimines are the four isomeric bidiazines (bdz) 3,3′-bipyridazine, 2,2′-bipyrazine, and 2,2′- and 4,4′-bipyrimidine,[6] the aromatic systems 2,2′-bipyridine (bpy), 1,4,7,10-tetraazaphenanthrene (tap), and η^2-2,2′,2″-terpyridine (terpy), and the nonaromatic α-diimines 1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene (dab) and 1,3-di-*tert*-butylsulfurdiimine (sdi) (Chart 1).

Coordination compounds between α-diimines and Re(CO)$_3$(Hal) have attracted attention because of their emission behavior,[6,7] because of their photochemistry involving electron transfer-active low-lying excited states, and because of their use in photo- or electrocatalytic processes aimed at CO_2 reduction.[8] Catalytic cycles proposed for the prototypical complex (bpy)Re(CO)$_3$Cl assumed the loss of axial CO or chloride ligands after the first electron uptake;[8b] however, EPR studies of the "19 valence electron Re(0)" complexes [(bpy)Re(CO)$_3$(Hal)]$^{-\bullet}$ rather indicated[9] an 18 + δ valence electron configuration at the metal and the preferential loss of axial halide ligands.[8h−j,9]

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

(1) (a) Olbrich-Deussner, B.; Kaim, W. *J. Organomet. Chem.* **1988**, *340*, 71. (b) Olbrich-Deussner, B.; Kaim, W. *J. Organomet. Chem.* **1989**, *266*, 155. (c) Kaim, W.; Olbrich-Deussner, B.; Gross, R.; Ernst, S.; Kohlmann, S.; Bessenbacher, C. In *Importance of Paramagnetic Organometallics Species in Activation, Selectivity and Catalysis*; Chanon, M., Ed.; Reidel: Dordrecht, The Netherlands, 1989; p 283.

(2) For further use of this concept see: (a) Brown, T. L. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; p 67. (b) Mao, F.; Tyler, D. R.; Bruce, M. R. M.; Bruce, A. E.; Rieger, A. L.; Rieger, P. H. *J. Am. Chem. Soc.* **1992**, *114*, 6418 and literature cited therein.

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

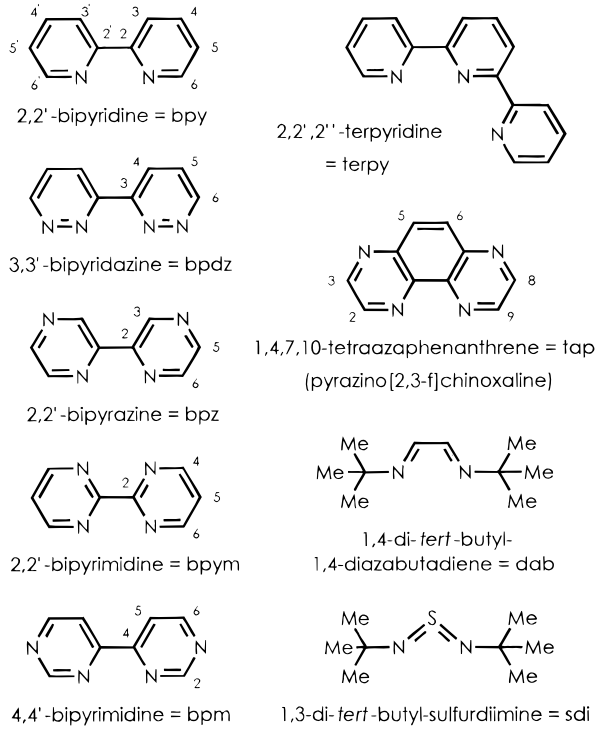
(4) Miholova, D.; Vlcek, A. A. *J. Organomet. Chem.* **1985**, *279*, 317.

(5) (a) Kaim, W.; Olbrich-Dessner, B. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 173. (b) Bruns, W.; Kaim, W.; Ladwig, M.; Olbrich-Deussner, B.; Roth, T.; Schwederski, B. In *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds*; Pombeiro, A. J. L., McCleverty, J., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993; p 255. (c) Coville, N. J. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; p 108.

(6) Kaim, W.; Kramer, H. E. A.; Vogler, C.; Rieker, J. *J. Organomet. Chem.* **1989**, *367*, 107 (the quantum yield for the bpm complex is 5 × 10^{-6} and not 5 × 10^{-1}, as misprinted).

0276-7333/96/2315-0236$12.00/0 © 1996 American Chemical Society

Chart 1



In order to identify which ligand properties determine the substitutional labilization after electron transfer, we now studied the EPR characteristics and the reactivity of the four isomeric bidiazine complexes $[(bdz)Re(CO)_3Cl]^{-\bullet}$.[6] The bidiazines,[6,10] the four symmetrical diaza-2,2′-bipyridine ligands, can be expected to yield fairly isostructural compounds closely related to the corresponding bpy complexes; however, the four bdz isomers are well suited to systematically study the electronic ligand influence of α-diimines[10] because they are distinctly different in their pK_{BH^+} values (bpy > bpdz > bpym > bpm > bpz), their reduction potentials and LUMO energies (bpm > bpz > bpdz ≈ bpym > bpy), and their π acceptor capability as measured by ^{14}N coupling constants of anion radicals or by calculated orbital coefficients c_N(LUMO) (bpdz ≈ bpz > bpy > bpym ≈ bpm).[10a,b] Complexes of bpy, tap, and η^2-terpy were studied because of their close relation to the bdz systems; the terpy complex had previously been formulated as $Re(\eta^3\text{-terpy})(CO)_2Cl$[11a] but could be identified later as $Re(\eta^2\text{-terpy})(CO)_3Cl$.[11b-d]

While the absorption and emission spectroscopy of the neutral precursors $(bdz)Re(CO)_3(Hal)$[6] and of corresponding bpy[7,8] and terpy[11a] complexes has been reported previously, the targets of this work are the reduced forms which should allow us to obtain at least a relative assessment of the δ in these "18 + δ" valence electron species and to correlate these results with the observed substitutional reactivity. These studies are complementary to a recent spectroelectrochemical investigation[12] which involved mainly α-diimine ligands with different imine functions. Complexes of the small, symmetrical, nonaromatic π acceptor ligands dab and sdi[11b,13] were studied because of their higher π acceptor capability[13,14] in comparison to the aromatic analogues. Considering the use of $(bpy)Re(CO)_3Cl$ as photo- or electrocatalyst for CO_2 reduction, we also studied the different EPR response of this much investigated system[8] under an argon and a CO_2 atmosphere.

Experimental Section

General Procedures and Syntheses. All syntheses and electrochemical and EPR manipulations were carried out in dried, redistilled solvents under an atmosphere of argon or CO_2 (see Figure 7).

The syntheses of the complexes $(bdz)Re(CO)_3(Hal)$, their spectroscopic characterization (NMR, IR, UV−vis absorption and emission), and their first reduction potentials were reported previously.[6] The complexes $(\alpha\text{-diimine})Re(CO)_3(Hal)$, α-diimine = bpy,[7] tap, terpy,[11] dab,[22] and sdi,[13b] were obtained accordingly from equivalent amounts of $Re(CO)_5(Hal)$ and the chelate ligand in refluxing toluene. After the CO evolution had ceased, the precipitated complexes formed upon cooling to room temperature were filtered out, washed with diethyl ether, and dried under vacuum (typical isolated yields 70%). Analytically pure (C, H, N) complexes were obtained after repeated dissolution in chloroform and careful crystallization or reprecipitation with *n*-hexane.

The ionic complexes $[(bdz)Re(CO)_3(CH_3CN)](PF_6)$[15] were obtained by treating solutions of $(bdz)Re(CO)_3Cl$ in refluxing

(7) (a) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (b) Shu, C. F.; Wrighton, M. S. *Inorg. Chem.* **1988**, *27*, 4326. (c) Vogler, A.; Kisslinger, J. *Inorg. Chim. Acta* **1986**, *115*, 13. (d) Worl, L. A.; Duesing, R.; Chen, P.; Della Ciana, L.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849. (e) Chen, P.; Duesing, R.; Graff, D. K.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 5850. (f) Van Wallendael, S.; Shaver, R. J.; Rillema, D. P.; Yoblinski, B. J.; Stathis, M.; Guarr, T. F. *Inorg. Chem.* **1990**, *29*, 1761. (g) George, M. W.; Johnson, F. P. A.; Westwell, J. R.; Hodges, P. M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2977. (h) Schanze, K. S.; MacQueen, D. B.; Perkins, T. A.; Cabana, L. A. *Coord. Chem. Rev.* **1993**, *122*, 63. (i) Kotch, T. G.; Lees, A. J.; Fuerniss, S. J.; Papathomas, K. I.; Snyder, R. *Inorg. Chem.* **1991**, *30*, 4871. (j) Stufkens, D. J. *Comments Inorg. Chem.* **1992**, *13*, 359. (k) Deschenaux, R.; Ruch, T.; Deschenaux, P.-F.; Juris, A.; Ziessel, R. *Helv. Chim. Acta* **1995**, *78*, 619. (l) Bardwell, D. A.; Barigelletti, F.; Cleary, R. L.; Flamigni, L.; Guardigli, M.; Jeffery, J. C.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 2438. (m) Yoblinski, B. J.; Stathis, M.; Guarr, T. F. *Inorg. Chem.* **1992**, *31*, 5. (n) Baiano, J. A.; Carlson, D. L.; Wolosh, G. M.; DeJesus, D. E.; Knowles, C. F.; Szabo, E. G.; Murphy, W. R., Jr. *Inorg. Chem.* **1990**, *29*, 2327.

(8) (a) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536. (b) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990. (c) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commu.* **1985**, 1414. (d) O'Toole, T. R.; Margerum, L. D.; Westmoreland, T. D.; Vining, W. J.; Murray, R. W.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1416. (e) Kutal, C.; Corbin, J.; Ferraudi, G. *Organometallics* **1986**, *6*, 553. (f) Hukkanen, H.; Pakkanen, T. T. *Inorg. Chim. Acta* **1986**, *114*, L43. (g) Breikss, A. I.; Abruña, H. D. *J. Electroanal. Chem.* **1986**, *201*, 347. (h) Christensen, P.; Hamnett, A.; Muir, A. V. G.; Timney, J. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1455. (i) Ziessel, R. In *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*; Kalyanasundaram, K., Grätzel, M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993; p 217. (j) Cosnier, S.; Deronzier, A.; Moutet, J.-C. *New J. Chem.* **1990**, *14*, 831.

(9) (a) Kaim, W.; Kohlmann, S. *Chem. Phys. Lett.* **1987**, *139*, 365. (b) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1990**, *29*, 2909.

(10) (a) Ernst, S.; Kaim, W. *J. Am. Chem. Soc.* **1986**, *108*, 3578. (b) Kaim, W.; Ernst, S. *J. Phys. Chem.* **1986**, *90*, 5010. (c) Ernst, S.; Kohlmann, S.; Kaim, W. *J. Organomet. Chem.* **1988**, *354*, 177. (d) Ernst, S. D.; Kaim, W. *Inorg. Chem.* **1989**, *28*, 1520. (e) Ladwig, M.; Kaim, W. *J. Organomet. Chem.* **1991**, *419*, 233. (f) Vogler, C.; Schwederski, B.; Klein, A.; Kaim, W. *J. Organomet. Chem.* **1992**, *436*, 367. (g) Vogler, C.; Kaim, W. *Z. Naturforsch.* **1992**, *47b*, 1057.

(11) (a) Juris, A.; Campagna, S.; Bidd, I.; Lehn, J.-M.; Ziessel, R. *Inorg. Chem.* **1988**, *27*, 4007. (b) Vogler, C. Ph.D. Thesis, University of Stuttgart, 1990. (c) Abel, E. W.; Long, N. J.; Orrell, K. G.; Osborne, A. G.; Pain, H. M.; Sik, V. *J. Chem. Soc., Chem. Commun.* **1992**, 303. (d) Civitello, E. R.; Dragovich, P. S.; Karpishin, T. B.; Novick, S. G.; Bierach, G.; O'Connell, J. F.; Westmoreland, T. D. *Inorg. Chem.* **1993**, *32*, 237.

(12) Stor, G. J.; Hartl, F.; van Outersterp, J. W. M.; Stufkens, D. J. *Organometallics* **1995**, *14*, 1115.

(13) (a) Stor, G. J.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1992**, *31*, 1319. (b) Mahabiersing, C.; de Lange, W. G. J.; Goubitz, K.; Stufkens, D. J. *J. Organomet. Chem.* **1993**, *461*, 127.

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

Table 1. Carbonyl Vibrational Frequencies ν(CO) of Rhenium(I) Complexes $[(L)Re(CO)_3X]^{n+}$ in Acetonitrile (cm^{-1})

L	X = Cl^-, $n = 0$	X = Br^-, $n = 0$	X = CH_3CN, $n = 1$	X = PPh_3, $n = 1$
bpy	2024, 1917, 1900	2025, 1920, 1909	2042, 1938 (br)	2042, 1957, 1927
terpy	2022, 1918, 1897			
bpdz	2028, 1932, 1907		2046, 1948 (br)	2040, 1938, 1922
bpm	2032, 1928, 1911	2022, 1927, 1910	2050, 1948 (br)	2052, 1968, 1938
bpz	2033, 1932, 1909	2033, 1933, 1917	2052, 1951 (br)	
tap	2033, 1938, 1907			
bpym	2035, 1928, 1910		2052, 1948 (br)	2045, 1965, 1932
dab	2022, 1912, 1901	2023, 1916, 1905		
sdi	2026, 1926, 1913	2027, 1928, 1917		

acetonitrile for 8 h with 1 equiv of $AgPF_6$. After cooling, the AgCl was filtered off and a saturated aqueous solution of NH_4PF_6 was added. Partial removal of the solvent under vacuum and addition of water gave light yellow precipitates which were collected and recrystallized from acetonitrile/water (1/2) to yield the hexafluorophosphate complexes in about 50% yield (satisfactory analyses; C, H, N). Long-wavelength absorption maxima λ (nm): 380 (bpdz complex), 381 (bpm complex), 373 (bpz complex), 365 (bpym complex).

The compounds $[(bdz)Re(CO)_3(PPh_3)](PF_6)$ could be prepared *in situ* from the corresponding acetonitrile complexes via established[14] thermal exchange reactions with PPh_3; i.e. by heating a mixture of the reactants for about 2 h in THF.[16] The exchange process can be monitored by IR spectroscopy (see Figure 1); however, complete conversion required an excess of PPh_3 (10 equiv) which could not be sufficiently removed from the ionic complexes.

Instrumentation. EPR: Bruker ESP 300 system in the X band. Radicals were generated electrolytically using a two-electrode cell,[17] and the spectra were analyzed with the help of computer simulations (Gaussian line forms, no corrections for second-order or variable line-width effects).[9] Substitution reactions of electrogenerated radical species for EPR monitoring are specified in the text (Results). IR: Perkin-Elmer 684 instrument. UV/vis/near-IR: Shimadzu UV 160 spectrophotometer. Cyclic voltammetry: Potentiostats M 173 or M 273 (PAR), function generator M 175 (PAR), three-electrode configuration with glassy carbon working electrode, Pt counter electrode, and SCE reference. The ferrocenium/ferrocene ($Fc^{+/0}$) couple served as reference in *N*,*N*-dimethylformamide (DMF) or acetonitrile solutions; the standard scan rate was 200 mV/s.

Results

The complexes $[(\alpha\text{-diimine})Re(CO)_3X]^n$, X = Cl^-, Br^- ($n = 0$) and X = CH_3CN, PPh_3 ($n = 1+$), were obtained via established substitution reactions.[6,7,11−13,15,16] They were characterized as *fac* isomers[7l,13,18,19] by their carbonyl vibrational spectra (Table 1) which exhibit a typical decrease in the splitting of the non-A_1 band along the series of axial substituents PPh_3 > halides (Cl^-, Br^-) > acetonitrile (Figure 1). With CH_3CN and one α-diimine vs three carbonyl ligands in *fac* configuration there seems to be an approximate C_{3v} spectroscopic symmetry, leading to a virtual "E" band (Figure 1).

For complexes with aromatic α-diimines, cyclic voltammetry at 200 mV/s in DMF showed electrochemically rather reversible first one-electron reduction processes ($i_{pa}/i_{pc} \geq 0.8$) and irreversible second reduction waves (Table 2; cf. Figure 3A). With the nonaromatic α-diimines, however, only $(dab)Re(CO)_3Cl$ exhibited reversible reduction at 200 mV/s in acetonitrile (Figure 2). The complexes $(dab)Re(CO)_3Br$ and $(sdi)Re(CO)_3(Hal)$ were irreversibly reduced under those conditions, but similar to $(dab)Re(CO)_3Cl$, they were found to

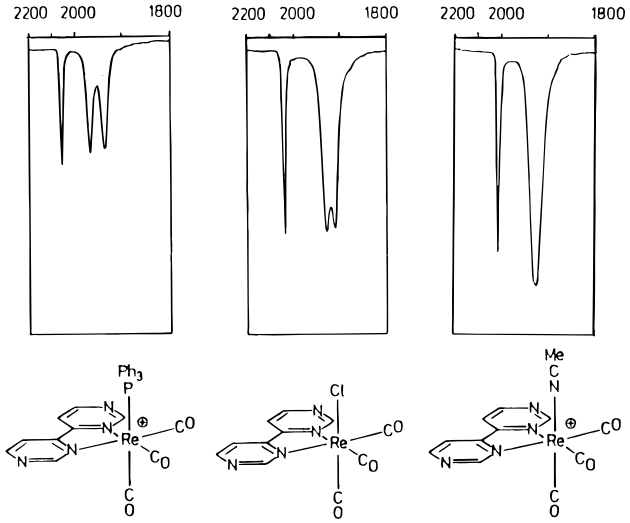


Figure 1. Carbonyl vibrational spectra of complexes $(bpm)Re(CO)_3X$ in CH_3CN solution.

Table 2. Electrochemical Data[a] for Rhenium(I) Complexes $[(L)Re(CO)_3X]^{n+}$

L	X	n	$E_{1/2}$(red1)	E_{pc}(red2)	$E_{1/2}$(ox)
bpy	Cl	0	−1.74 (70)	−2.20	
bpy	Br	0	−1.73 (90)	−2.14	
terpy	Cl	0	−1.75 (60)	−2.24	
bpdz	Cl	0	−1.39 (70)[d]	−1.91	
bpdz[b]	CH_3CN	1	−1.30 (65)	−1.73	
bpm	Cl	0	−1.10 (75)[e]	−1.71	
bpm	Br	0	−1.08 (70)	−1.65	
bpm[b]	CH_3CN	1	−1.08 (90)	−1.56	
bpz	Cl	0	−1.23 (75)[f]	−1.67	
bpz	Br	0	−1.23 (100)	−1.74	
bpz	CH_3CN	1	−1.07 (80)	−1.65	
tap	Cl	0	−1.18 (65)	−1.73	
bpym	Cl	0	−1.42 (80)[g]	−2.04	+0.96 (200)[b,c]
bpym	CN	0	−1.42 (120)	−2.12 (120)[h]	
bpym[b]	CH_3CN	1	−1.38 (70)	−1.74	
bpym	PPh_3	1	−1.29 (100)	−1.83	
dab[b]	Cl	0	−1.43 (60)	−2.03	+1.05 (80)
dab[b]	Br	0	−1.40 (E_{pc})		+1.02 (80)
sdi[b]	Cl	0	−1.10 (E_{pc})		+1.03 (100)
sdi[b]	Br	0	−1.22 (E_{pc})		+1.00 (100)

[a] From cyclic voltammetry in DMF/0.1 M Bu_4NClO_4, unless stated otherwise. Potentials in V vs $Fc^{+/0}$; peak potential differences in mV (in parentheses). Scan rate 200 mV/s. E_{pc}: cathodic peak potential for irreversible process. [b] In acetonitrile/0.1 M Bu_4NClO_4. [c] At 20 V/s scan rate. [d] $i_{pa}/i_{pc} = 0.81$. [e] $i_{pa}/i_{pc} = 0.95$. [f] $i_{pa}/i_{pc} = 0.80$. [g] $i_{pa}/i_{pc} = 0.90$. [h] Quasi-reversible wave (Figure 3D).

(15) Cf.: Leasure, R. M.; Sacksteder, L. A.; Nesselrodt, D.; Reitz, G. A.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1991**, *30*, 3722.
(16) Summers, D. P.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 5238.
(17) Kaim, W.; Ernst, S.; Kasack, V. *J. Am. Chem. Soc.* **1990**, *112*, 173.
(18) (a) Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1995**, *14*, 2387. (b) See also: Cheng, C. P.; Wang, S. R.; Lin, J. C.; Wang, S.-L. *J. Organomet. Chem.* **1988**, *249*, 375.
(19) Cf.: Rossenaar, B. D.; Kleverlaan, C. J.; van de Ven, M. C. E.; Stufkens, D. J.; Oskam, A.; Fraanje, J.; Goubitz, K. *J. Organomet. Chem.* **1995**, *493*, 153.

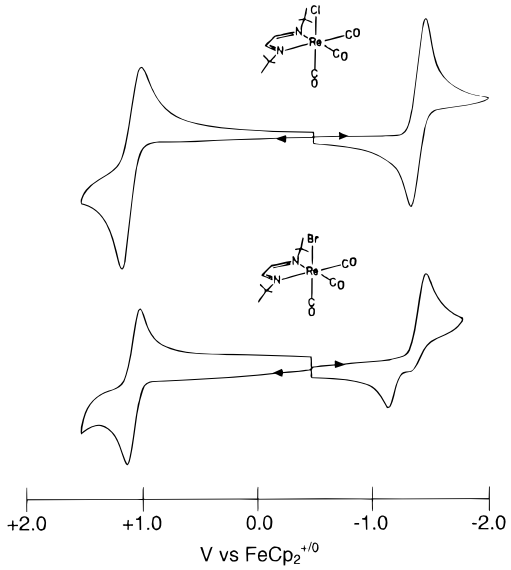


Figure 2. Cyclic voltammograms of complexes (dab)Re(CO)$_3$(Hal) in acetonitrile/0.1 M Bu_4NClO_4 at 200 mV/s.

undergo a reversible one-electron oxidation (Figure 2). In contrast, the complexes with aromatic α-diimines showed generally irreversible oxidation waves between 0.9 and 1.2 V vs $Fc^{+/0}$ in either DMF or CH_3CN; these can become reversible only at rather high scan rates in less nucleophilic acetonitrile (Table 2).[20]

The second reduction is always irreversible, even for the least labile system (bpm)Re(CO)$_3$Cl at 20 V/s scan rate. Chloride was detected as a dissociation product via oxidation.[8g]

In the presence of excess axial ligands, the cyclic voltammograms show characteristic changes, as illustrated in Figure 3 by example of the (bpym)Re(CO)$_3$X system: Whereas an excess of chloride (Figure 3B) causes slightly shifted and increasingly reversible reduction waves of (bpym)Re(CO)$_3$Cl, the addition of PPh_3 produces new, anodically shifted waves after the first reduction scan which are attributed to the substituted species (Figure 3C). Despite the presence of excess triphenylphosphine, these new waves remain relatively small, indicating an unfavorable exchange equilibrium under those conditions (i.e. in DMF solution). In contrast, the addition of excess anionic cyanide produces immediately two reversible waves with only a small wave of the chloride complex left (Figure 3D).

The relative stability of many one-electron reduced "Re(0)" states of the α-diimine complexes at convenient potentials $E > -2.0$ V (Table 2) prompted us to study these states and their exchange reactions by EPR (Table 3). Although these states are expectedly[3,21,22] better described as radical complexes[9] (α-diimine$^-$)Re^{I} than as "Re(0)" species,[8b] the large magnetic moments of the two relevant rhenium isotopes ^{185}Re ($I = {}^5/_2$, 37.4% natural abundance; nuclear magnetic moment +3.187 β_N) and ^{187}Re ($I = {}^5/_2$, 62.6%; +3.20 β_N) provide usually sufficient information via the metal hyperfine coupling. However, the presence of the heavy 5d^6 center Re(I) often causes broad lines which may obscure α-diimine ligand hyperfine splitting, especially if the ancillary axial ligands have coupling nuclei with small magnetic moments, such as ^{14}N or the halide isotopes. Figure 4 illustrates this situation by example of radical complexes [(bpdz$^-$)Re^{I}(CO)$_3$X]^n.

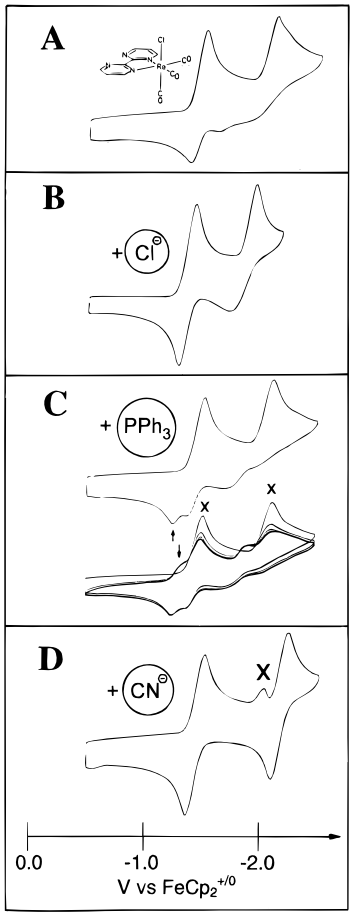


Figure 3. Cyclic voltammograms of complex (bpym)Re(CO)$_3$Cl at 200 mV/s in DMF/0.1 M Bu_4NClO_4 (A), in the presence of 0.1 M Et_4NCl (B), after addition of 5 equiv of PPh_3 (single- and multisweep experiment) (C), and after addition of 5 equiv of Et_4NCN (D). Waves of the chloride complex are indicated (×) in the cyclic voltammograms (C) and (D).

In the anionic chloride complex, the halide apparently exhibits some unresolved hyperfine coupling (^{35}Cl, $I = {}^3/_2$, 75.77%, +0.822 β_N; ^{37}Cl, $I = {}^3/_2$, 24.23%, 0.684 β_N) which typically broadens the spectrum to a considerable extent (Figure 4A). With acetonitrile as axial ligand (^{14}N, $I = 1$, 99.63%, +0.404 β_N), there is better resolution, at least of the (increased) metal isotope coupling (Figure 4B). The best resolution is obtained for [(bpdz)Re(CO)$_3$(PPh$_3$)]$^\bullet$, where there is significantly increased ^{185,187}Re and additional ^{31}P hyperfine splitting ($I = {}^1/_2$, 100%, 1.132 β_N) but no other significant broadening effect; parts of the α-diimine ligand hyperfine coupling are therefore resolved (Figure 4C; Table 3). In comparison to other metal complexes of the α-diimine anion radicals,[10b,14,22,23] the observed hyperfine splittings of the chelate ligands can easily be identified and assigned (Table 3).

On the basis of the electrochemical and EPR results, we then carried out *in situ* EPR-spectroelectrochemical

(20) Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790.

(21) Creber, K. A. M.; Ho, R. I.; Depew, C.; Weir, D.; Wan, J. K. S. *Can. J. Chem.* **1982**, *60*, 1504.

(22) Andrea, R. R.; de Lange, W. G. J.; van der Graf, T.; Rijkhoff, M.; Stufkens, D. J.; Oskam, A. *Organometallics* **1987**, *7*, 1100.

(23) Hunter, J. A.; King, B.; Lindsell, W. E.; Neish, H. A. *J. Chem. Soc., Dalton Trans.* **1980**, 880.

Table 3. EPR Data[a] for Complexes $[(L^-)Re^I(CO)_3X]^{n-}$

L	X	*n*	*g*	$a^{(185,187}$Re)	$a(^{31}$P)	$a(^{14}$N)	$a(^{1}$H)
bpy	Cl	1	2.0032	1.2		n.o.	
bpy	CH_3CN	0	2.0033	2.2		n.o.	
bpy[b]	CO_2	0	2.0010	1.6		n.o.	
bpy	PPh_3	0	2.0018	2.0	2.0	n.o.	
terpy	Cl	1	2.0025	1.0		n.o.	
terpy	PPh_3	0	2.0018	2.0	2.0	n.o.	
bpdz	Cl	1	2.0018	1.4		n.o.	
bpdz	CH_3CN	0	n.d.	1.82		n.o.	
bpdz	PPh_3	0	2.0003	3.6	3.6	0.58 (N2)	0.29 (H5)
bpm	Cl	1	2.0028	0.8		n.o.	
bpm	PPh_3	0	2.0007	2.1	2.1	n.o.	
bpz	Cl	1	2.0023	1.6		n.o.	
bpz	PPh_3	0	2.0010	3.1	3.1	0.5 (N1)	0.5 (H5)
bpz[c]	PPh_3	0	2.0000	3.8	1.7	0.5 (N1)	0.5 (H5)
tap	Cl	1	2.0003	1.6		n.o.	
bpym	Cl	1	2.0026	1.0		n.o.	
bpym	PPh_3	0	2.0010	2.8	2.8	n.o.	
dab	Cl	1	2.0032	1.9			
dab	CH_3CN	0	n.d.	3.72		0.73	0.45
dab	PPh_3	0	2.0013	4.07	4.07	0.72	0.44
dab[d]	PPh_3	0	2.0047	3.973	3.973	0.740	0.445
dab[d]		0	2.0036	3.561		0.726	0.465
sdi	PPh_3	0	2.0014	1.53	4.18	0.68	n.o.
sdi		0	2.0009	2.19		0.68/0.50[e]	n.o.

[a] Coupling constants *a* in mT, radical generation via (electro)-chemical reduction in THF/0.1 M Bu_4NClO_4. [b] From radical generation in CH_3CN/0.1 M Bu_4NPF_6 under a CO_2 atmosphere. [c] Secondary radical (see text). [d] From photolysis experiments in benzene, reported in ref 22. [e] From partially analyzed spectrum.

experiments in which 10^{-3} M solutions of the isomeric anion radicals $[(bdz)Re(CO)_3Cl]^-$ were obtained by careful electrolysis in THF/0.1 M Bu_4NClO_4 and then treated with an excess (0.01 M) of PPh_3. The following was observed: (i) The complex $[(bpm)Re(CO)_3Cl]^{-\bullet}$ with $a(^{185,187}Re) = 0.8$ mT did not show any sign of substitution, even after 30 min. (ii) The radical anion $[(bpym)Re(CO)_3Cl]^{-\bullet}$ with $a(^{185,187}Re) = 1.0$ mT showed slow substitution within tens of minutes; both substituted and unsubstituted radical complexes are visible in different ratios (Figure 5). (iii) The radical complexes $[(bpdz)Re(CO)_3Cl]^{-\bullet}$ with $a(^{185,187}Re) = 1.4$ mT and $[(bpz)Re(CO)_3Cl]^{-\bullet}$ with $a(^{185,187}Re) = 1.6$ mT exchange immediately after addition of PPh_3; the chloride-containing anion radicals are not observable under these conditions.

The latter behavior is also found for the complexes of dab and sdi, if the systems (α-diimine)$Re(CO)_3$(Hal) are reduced in the presence of PPh_3 (Figure 6). In the case of $[(dab)Re(CO)_3(PPh_3)]^\bullet$ we could essentially reproduce the EPR parameters reported before[22] for the photogenerated species; however, the *g* factor was found to be lower, more in agreement with the data of all other such radical complexes (Table 3).[9,21] Irreversible chemical reduction of $(sdi)Re(CO)_3Cl$ alone yielded a paramagnetic species which could not be fully analyzed by EPR. Following the presentation of photogenerated $[(dab)Re(CO)_3]^\bullet$ radicals by Stufkens and co-workers,[22] we tentatively assume a possibly solvated species $[(sdi)Re(CO)_3]^\bullet$. $16 + \delta$ valence electron species should be stable if a strong π donor ligand such as a catecholate[24] or a reduced small heterocycle[25] can compensate for the formal lack of valence electrons.

After substitution of Cl^- by PPh_3, the bidiazine complex with the largest rhenium hyperfine coupling,

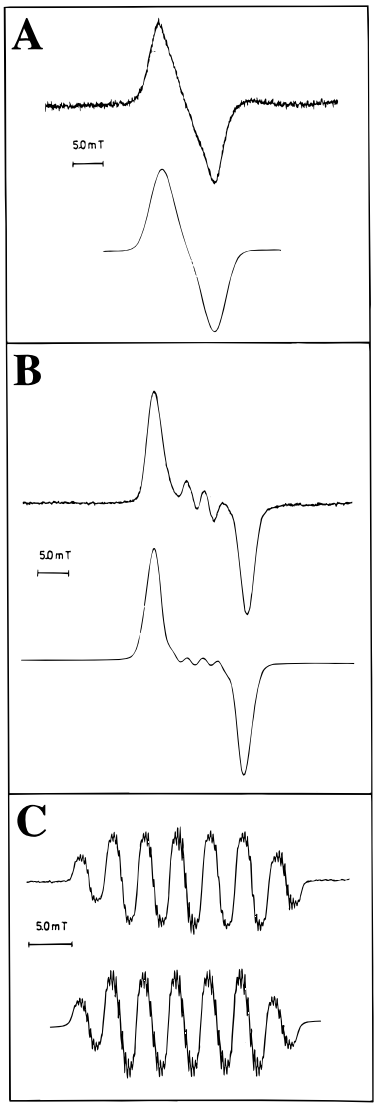


Figure 4. EPR spectra of complexes $(bpdz^{-\bullet})Re(CO)_3X$, generated from precursors by cathodic reduction in THF/0.1 M Bu_4NClO_4, with respective computer simulations: X = Cl^- (A); X = CH_3CN (B); X = PPh_3 (C).

i.e. $[(bpz)Re(CO)_3(PPh_3)]^\bullet$, reacts slowly further to yield after 2 h a new radical complex with diminished ^{31}P coupling and increased metal hyperfine splitting (Table 3).

In view of detailed IR-spectroelectrochemical[8h] and other studies of the CO_2 activation by $(bpy)Re(CO)_3Cl$ and related complexes,[8] we investigated the EPR behavior of this compound under reducing conditions in the presence of a CO_2 atmosphere. The reduction was carried out at a Pt cathode in acetonitrile containing 0.1 M Bu_4NPF_6; changes in the EPR spectra were monitored after suitable time intervals.

Starting with the typical "two-line" appearance of the spectrum of $[(bpy)Re(CO)_3Cl]^{-\bullet}$ with small ^{185,187}Re coupling,[9] that anion radical complex reacts to eventually produce new species with larger metal hyperfine splitting (Figure 7).

Irrespective of the presence of CO_2, the first two EPR spectra (Figure 7A,B) observed after cathodic reduction

(24) (a) Hartl, F.; Vlcek, Jr., A.; deLearie, L. A.; Pierpont, C. G. *Inorg. Chem.* **1990**, *29*, 1073. (b) Darensbourg, D. J.; Klausmeyer, K. K.; Mueller, B. L.; Reibenspies, J. H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1503.

(25) (a) Bruns, W.; Hausen, H.-D.; Kaim, W.; Schulz, A. *J. Organomet. Chem.* **1993**, *444*, 121. (b) Bruns, W.; Kaim, W.; Waldhör, E.; Krejcik, M. *Inorg. Chem.* **1995**, *34*, 663. (c) Hilgers, F.; Bruns, W.; Fiedler, J.; Kaim, W. *J. Organomet. Chem.*, in press.

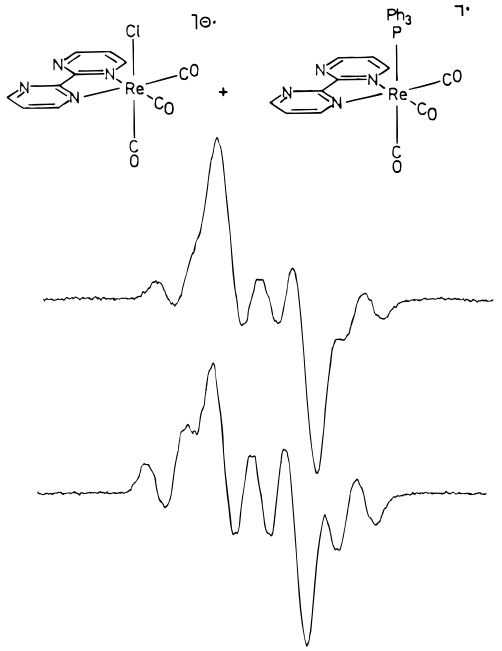


Figure 5. EPR spectra observed following the reaction in THF of electrogenerated $[(bpym)Re(CO)_3Cl]^{-\bullet}$ with excess PPh_3 (ca. 10 equiv) after 10 (top) and 30 min (bottom).

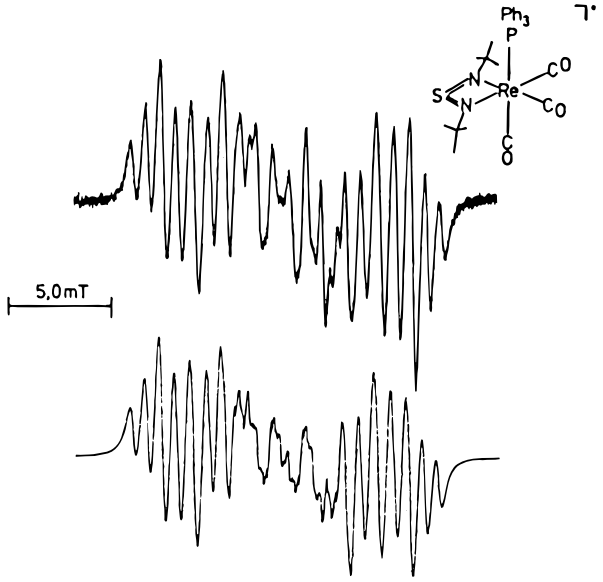


Figure 6. Top: EPR spectrum of $(sdi^{-\bullet})Re(CO)_3(PPh_3)$, generated by cathodic reduction of $(sdi)Re(CO)_3Br$ in the presence of excess PPh_3 (about 5 equiv) in THF/0.1 M Bu_4NClO_4. Bottom: Simulated spectrum calculated with the data from Table 3.

illustrate the conversion of $[(bpy)Re(CO)_3Cl]^{-\bullet}$ [9a] to a species which has lost the chloride ligand.[9b] Only under CO_2 atmosphere, a third radical species appears (Figure 3C) which then undergoes further conversion with time; identification of the various paramagnetic follow-up products will be attempted, employing the range of conceivable[8h−j] intermediates.

Discussion

Most chelate complexes $[(\alpha\text{-diimine})Re(CO)_3X]^{n+}$ of Table 2 are apparently reduced reversibly in the cyclic voltammetric experiment, except for $(dab)Re(CO)_3Br$ and both complexes $(sdi)Re(CO)_3(Hal)$. This observation already suggests that it is not the first reduction

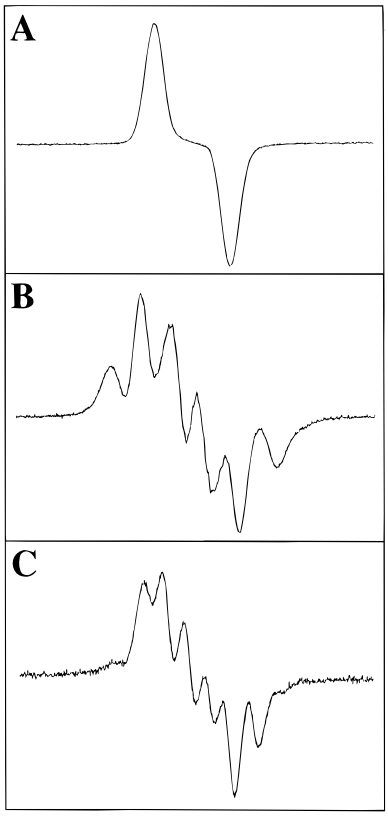


Figure 7. EPR spectra observed following the cathodic reduction of $(bpy)Re(CO)_3Cl$ in CH_3CN/0.1 M Bu_4NPF_6 under a CO_2 atmosphere after 1 min (A), 10 min (B), and 20 min (C). Spectra A and B were also obtained during a control experiment under argon and are identified as $(bpy^{-\bullet})Re(CO)_3X$, X = Cl (A) and X = CH_3CN (B).

potential $E_{1/2}$(red1) of the complexes, increasing in the typical[10,14,23] ligand order (eq 1) for chloride complexes, but the additional electron density transmitted from the π system of the primarily reduced α-diimine ligand to the parallel[1c,71,9,18,19] Re−Hal bond which labilizes the halide.

$E_{1/2}$(red1):

$$\xrightarrow[\text{(increasingly facile reduction)}]{\text{terpy} \approx \text{bpy} < \text{dab} \approx \text{bpym} < \text{bpdz} < \text{bpz} < \text{tap} < \text{bpm} \approx \text{sdi}} \quad (1)$$

Exchange of the halide following one-electron reduction is evident from the ^{31}P hyperfine coupling appearing in the EPR spectra of triorganophosphine-substituted anion radical complexes. Under the conditions employed, the smallest (i.e. 3 center) π system sdi exhibits the most pronounced halide labilization despite a facile reduction, whereas the 4-center π system dab shows lability only for the bromide but not for the chloride derivative. A more quantitative measure of the amount of spin density transferred via spin polarization and π/σ hyperconjugation[1c,9] from the α-diimine anion radical to the organometallic fragment are the metal and the ^{31}P hyperfine coupling constants in correspondingly substituted species which increase along the series in (2).

$$\text{bpm} < \text{bpym} < \text{bpz} < \text{bpdz} < \text{dab} \approx \text{sdi} \quad (2)$$

In unperturbed complexes of the $[Re(CO)_3(PPh_3)]^+$ fragment the $^{185,187}Re$ and ^{31}P hyperfine coupling con-

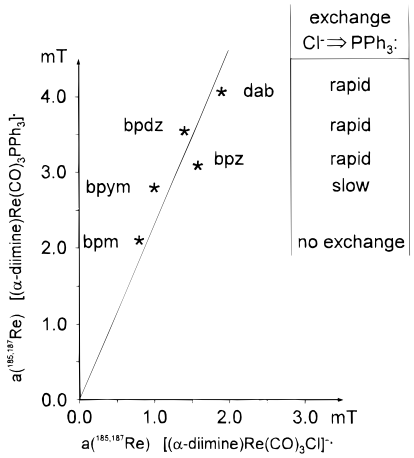


Figure 8. Correlation of ^{185,187}Re hyperfine coupling constants for complexes [(α-diimine)Re(CO)$_3$Cl]$^{-\bullet}$ and [(α-diimine)Re(CO)$_3$(PPh$_3$)]$^{\bullet}$.

stants are often of a similar magnitude;[21,22] the exceptions encountered here are the secondary radical of the bpz complex with an unusually small ^{31}P coupling and the radical species obtained from the sdi system with a diminished metal hyperfine splitting (Table 3). Diminished ^{31}P coupling could be due either to a *fac* → *mer* isomerization where the PPh$_3$ ligand would come to lie in the π plane[3,26] or to a dissociation of CO to form a five-coordinated 16 + δ valence electron species.[25] The small metal splitting of the sdi radical complexes may result from altered spin transfer in the strained four-membered chelate[27] ring N−S−N−Re. Another explanation would be different hapticity and resulting lower symmetry; this alternative is suggested by the appearance of two slightly different ^{14}N splittings in the complex tentatively identified as [(sdi)Re(CO)$_3$]$^{\bullet}$ which results form irreversible reduction of (sdi)Re(CO)$_3$Cl. In a good approximation, the ^{185,187}Re coupling increases by a factor of 2.2 on exchanging the π donor ligand Cl$^-$ by π-accepting PPh$_3$ in (α-diimine)Re(CO)$_3$ radical complexes. Figure 8 shows this correlation together with the chemical consequences, i.e. the reductive labilization of the metal/halide bond. In contrast to (bpz)Re(CO)$_3$Br, (dab)Re(CO)$_3$Br is no longer reduced reversibly, in agreement with the correlation in Figure 8.

Since it may be argued that ring size effects and the nonaromatic nature make complexes of the sdi ligand special, we shall focus our discussion now particularly on the four isomeric complexes (bdz)Re(CO)$_3$X. While there are no significant differences in the reduction potentials of corresponding chloride and bromide complexes, the cationic acetonitrile complexes are reduced at slightly less negative potentials, supported by the positive charge. With PPh$_3$ as axial ligand, the reduction is facilitated still further. The EPR coupling constants of the metal are particularly small for the halide-containing radical complexes due to some spin delocalization to the halide nuclei;[9] this interpretation is in agreement with the rather low resolution of such spectra which would be one of the consequences of unresolved halide hyperfine coupling. The conspicuous lowering of *g* factors in the case of triorganophosphine-substituted radical complexes is a familiar phenomenon[1,3,21,25,28] which can be attributed to the presence of low-lying unoccupied orbitals at those ancillary ligands.

In the series of the chloride complexes of aromatic α-diimines, the first one-electron reduction processes seem always reversible. However, when one looks carefully at the current ratios i_{pa}/i_{pc} for the four isomeric bidiazine complexes (under otherwise identical conditions), the values deviate increasingly from 1.0 (Table 2) in the order of ligands in (3), indicating increasing reactivity of the electrogenerated monoanions.

$$\text{bpm} < \text{bpym} < \text{bpdz} \approx \text{bpz} \qquad (3)$$

This sequence which is the same as that of calculated and experimental π spin populations at the coordinating nitrogen atoms or at coordinated nuclei[10] (Figure 8) has been encountered again in the *in situ* EPR substitution experiment outlined under Results.

Assuming eqs 4 and 5 for the primary processes,[8h-j] we thus conclude that one−electron reduced species

$$(\alpha\text{-diimine}^0)\text{Re}^{\text{I}}(\text{CO})_3\text{Cl} + e^- \rightleftharpoons [(\alpha\text{-diimine}^-)\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}]^{-\bullet} \qquad (4)$$

$$[(\alpha\text{-diimine}^-)\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}]^{-\bullet} + \text{L} \rightleftharpoons [(\alpha\text{-diimine}^-)\text{Re}^{\text{I}}(\text{CO})_3\text{L}]^{\bullet} + \text{Cl}^- \qquad (5)$$

which have α-diimine ligands with large π SOMO (singly occupied molecular orbital) coefficients and EPR hyperfine coupling constants at the coordinating nitrogen centers such as sdi,[23] dab,[14] bpz, or bpdz[10b] can transmit larger amounts of charge "δ" to the metal, as illustrated by large ^{185,187}Re hyperfine splitting (Table 3; Figure 8), and hence to the metal−halide bond. The result of this sizable population of an antibonding Re-Hal σ orbital[1c,9] is an increased activation toward substitution.

In other cases, such as with bpym and especially bpm as ligands, the amount δ of charge that can be transferred from the π SOMO of the reduced α-diimine via the coordinating nitrogen centers at the ligand−metal interface is smaller, as evident from the EPR data (Table 3; Figure 8) and from calculations of the free ligand radicals.[10b] Accordingly, the activation of the metal−halide bond decreases. When the unpaired electron is predominantly localized in a noncoordinating part of the molecule like in the anion radical of 2,3-bis(diphenylphosphino)maleic anhydride (bma),[2b] then the reduced tricarbonylrhenium halide complexes can even become sufficiently stable for isolation and crystallographic characterization, as reported for [(bma)Re(CO)$_3$Br][CoCp$_2$].[18a] This latter example as well as the *systematic* studies presented here for a series of structurally related symmetrical complexes (α-diimine)Re(CO)$_3$Cl confirm that the reduction potential or the size of the noninnocent ligand alone cannot be correlated at all with the observed reactivity. In addition to structural effects, especially for systems with different imine or azo functions,[12] *the amount δ of charge transferred from the noninnocent ligand via the metal to the halide determines its labilization.*

(26) Alberti, A.; Camaggi, C. M. *J. Organomet. Chem.* **1979**, *181*, 355.
(27) Meij, R.; Olie, K. *Cryst. Struct. Commun.* **1975**, *4*, 515.
(28) Kaim, W. *J. Organomet. Chem.* **1984**, *262*, 171.

Oxidation of the (α-diimine)$Re(CO)_3Cl$ complexes is usually irreversible unless rapid scan voltammetry is employed;[20] experiments on the bpym complex confirmed this notion (Table 2). However, the compounds of the nonaromatic α-diimines exhibit reversible one-electron oxidation features (Figure 2) albeit at rather positive potentials (Table 3); variable-temperature EPR studies will have to substantiate the assumed Re(II) = $5d^5$ configuration[29] of these cationic species. As for the lability of the anionic states of these complexes with sdi or dab, the reason for the stability of the *cations* cannot be the (little changed) redox potential but a slowing of breakdown reactions such as the loss of CO.

With respect to the non-bidiazine aromatic ligands, it is obvious from Tables 2 and 3 that bpy and terpy complexes are rather similar, supporting the η^2-binding mode of potentially tridentate terpy to the thermally rather stable $Re(CO)_3Cl$ configuration.[11b−d] The reduction of coordinated terpy is reversible in contrast to that of the free ligand.[30] The complex of tap shows much similarity with the bpz complex, as can be expected from the comparable nitrogen substitution pattern.[11b,31]

Addition of nucleophiles and potentially better ligands for the partially negatively charged rhenium center in the 18 + δ valence electron complexes produces characteristic electrochemical responses (Figure 3): First, the addition of excess chloride causes an improved reversibility of both the first and the second reduction process (Figure 3B), confirming the equilibrium nature of the electrode-induced dissociative labilization of the halide (EC process, (4) and (5)). While basic triphenylphosphine does not substitute to a very large extent and requires prereduction before substitution (Figure 3C), cyanide ligands replace the chloride much easier, causing increased reversibility of both reduction waves (Figure 3D). This stability of $Re(CO)_3(CN)$ toward reductive dissociation is due to the poor leaving-group character of CN^- and has already been employed for the generation of the mixed-valent species $\{(Re^{VI}S_4)[Re^{I}(CO)_3(CN)]_2\}^{2-}$.[32]

The half-wave potentials measured for reversible oxidation *and* reduction processes in the case of the compounds (dab)$Re(CO)_3Cl$ and (bpym)$Re(CO)_3Cl$ can be used to estimate reorganization energies following the respective low-energy electronic transitions. In a very approximative[33] approach,[10a,d,34,35] the energy E_{op} (in eV) at the absorption maximum of the long-wavelength optical transition can be correlated with the potential difference $E_{red1} - E_{ox1} = \Delta E_{red/ox}$ (in V) according to (6), where χ accounts for the contributions from intra- and intermolecular reorganization following Franck−Condon excitation.

$$E_{op} - \Delta E_{red/ox} = \chi \qquad (6)$$

Complexes (α-diimine)$Re(CO)_3Cl$ display well discernible metal-to-ligand charge transfer (MLCT) absorption bands in the visible,[6,7,13] and the corresponding excited states participate in the widely studied[6,7] luminescence behavior and photochemistry of these materials. For instance, the complexes of the nonaromatic α-diimines dab and sdi exhibit typical[36] MLCT bands in the visible which are intense (ϵ 2000−5000 M^{-1} cm^{-1}), broad ($\Delta\nu_{1/2}$ 4000−6000 cm^{-1}) and negatively[37] solvatochromic; i.e. they show a bathochromic shift when going from polar to less polar solvents: ν_{max}(acetonitrile/toluene) 24 390/22 270 cm^{-1} for (dab)$Re(CO)_3Cl$, 23 980/21 930 cm^{-1} for (dab)$Re(CO)_3Br$, 21 980/20 200 cm^{-1} for (sdi)$Re(CO)_3$-Cl, and 21 650/20 040 cm^{-1} for (sdi)$Re(CO))_3Br$.

When the absorption maxima at 24 390 cm^{-1} = 3.02 eV for (dab)$Re(CO)_3Cl$ or 26 300 cm^{-1} = 3.26 eV for (bpym)$Re(CO)_3Cl$[6] are contrasted with the corresponding redox potential differences $\Delta E_{red/ox}$ of 2.38 V (dab complex) or 2.48 V (bpym complex) in polar acetonitrile (Table 2), the values χ come out as rather large[33b,c] with 0.64 (dab complex) and 0.78 eV (bpym complex). The reason could be extensive structural reorganization in these nonchelate complexes on MLCT excitation or a difference between the target orbitals of the (electro)-chemical reduction and the low-energy optical transition. In fact, detailed photophysical studies suggest the participation of low-lying ligand-field (LF) states in the actual photochemistry of these compounds.[7] However, we do not favor the latter alternative since the χ values of α-diimine complexes with tetracarbonylchromium(0)[10a] or diorganoplatinum(II) species[35] lie in a similar range. Moreover, when the average is calculated for the energies at the maxima of electronic absorption (3.26 eV) and emission (1.71 eV)[6] for (bpym)$Re(CO)_3Cl$, the resulting value of 2.485 eV agrees perfectly with $\Delta E_{red/ox}$ = 2.48 V. The lower χ value for the dab analogue may not only reflect a decreased number of freedom of the smaller system but also a diminished MLCT character of the electronic transition.[38]

The electrochemical reduction of CO_2 to CO as catalyzed by (bpy)$Re(CO)_3Cl$ and derivatives has recently been interpreted on the basis of spectroelectrochemical studies.[8h] Following the initial activation (eq 4) to the halide-containing radical complex (see Figure 7A), one may assume a certain extent of exchange (eq 5) with the solvent = L, here the potentially coordinating acetonitrile. The consequences for the EPR spectrum (Figure 7B) are an improved resolution due to the absence of small but line-broadening $^{35,37}Cl$ hyperfine coupling and an increase in the metal hyperfine splitting from 1.2 to 2.2 mT. These changes illustrate clearly that the metal−halide bond participates to a non-negligible extent at the SOMO which, however, cannot be described in terms of a Re(0) formulation.[8b,39] In the presence of CO_2, there is an additional exchange reaction of the secondary paramagnetic species which we interpret as the substitution of solvent by CO_2 (eq 7).

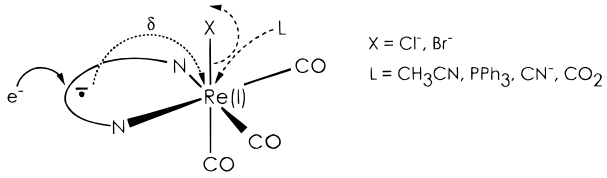
(29) (a) Matondo, S. O. C.; Mountford, P.; Watkin, D. J.; Jones, W. B.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1995**, 161. (b) Lever, A. B. P. *Inorg. Chem.* **1991**, *30*, 1980 and literature cited.
(30) Rao, J. M.; Hughes, M. C.; Macero, D. J. *Inorg. Chim. Acta* **1976**, *16*, 231.
(31) Kirsch-De Mesmaeker, A.; Nasielski-Hinkens, R.; Maetens, D.; Pauwels, D.; Nasielski, J. *Inorg. Chem.* **1984**, *23*, 377.
(32) Schäfer, R.; Kaim, W.; Fiedler, J. *Inorg. Chem.* **1993**, *32*, 3199.
(33) (a) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam 1984; p 776. (b) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1985**, *119*, 61. (c) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1986**, *124*, 152.
(34) (a) Kober, E. M.; Goldsby, K. A.; Narayana, D. N. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4303. (b) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.
(35) Klein, A.; Kaim, W. *Organometallics* **1995**, *14*, 1176.
(36) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.
(37) (a) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, Germany, 1988. (b) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 3825. (c) Kaim, W.; Kohlmann, S.; Ernst, S.; Olbich-Deussner, B.; Bessenbacher, C.; Schulz, A. *J. Organomet. Chem.* **1987**, *321*, 215.
(38) Stufkens, D. J. *Coord. Chem. Rev.* **1990**, *104*, 39.

$$[(\alpha\text{-diimine}^-)Re^I(CO)_3L]^\bullet + CO_2 \rightleftharpoons [(\alpha\text{-diimine}^-)Re^I(CO)_3(CO_2)]^\bullet + L \quad (7)$$

The EPR spectrum of this primary paramagnetic product of reaction with CO_2 is distinguished by an intermediate ^{185,187}Re coupling constant, indicating a moderate metal-to-CO_2 spin transfer. Quite revealing is the lowered g value (2.0033 → 2.0010) which is similar to that of triorganophosphine-substituted species (Table 3) and which suggests the presence of a ligand with relatively low-lying unoccupied molecular orbitals. It is conceivable that the thus transferred π spin density from the α-diimine ligand via the metal to the π system of coordinated CO_2[40] contributes to its reduction to CO after additional electrophilic attack by H^+; the established[9,10g] strong σ acceptor capability of tricarbonylrhenium(I) serves to initially bind and preactivate the inert carbon dioxide molecule. The primary paramagnetic complex of the reaction (7) with CO_2 is replaced by other species within minutes, as evident from changing EPR spectra; their identification (formiate, hydride, carbonyl complexes?)[7] and the significance of these results are under investigation.

Summary. In the above rhenium and related ruthenium, iridium, or rhodium[8i,41] complexes which can serve as electrocatalysts for substrate reduction, the noninnocent α-diimine ligands can act as active electron buffers for what is in effect the catalysis of a two-electron process. In connection with the variable and EPR-detectable overlap between the π* orbital of the α-diimine and the σ(Re−Hal) antibonding orbital, the predominant but not complete localization of the added electron in the α-diimine π system (18 + δ valence electron situation) can result in reversible dissociation of halide ligands, thus producing the necessary coordinatively unsaturated intermediate forms. At the same time, however, the metal centers in such complexes (here $Re^{I-\delta}$) may remain sufficiently electrophilic to bind a number of substrates L (Scheme 1).

Scheme 1



Note Added in Proof: A related paper on the correlation between δ and the reactivity in 18 + δ complexes has appeared recently: Schut, D. M.; Keana, K. J.; Tyler, D. R.; Rieger, P. H. *J. Am. Chem. Soc.* **1995**, *117*, 8939.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and Stiftung Volkswagenwerk for generous support of this work.

OM950500E

(39) For a genuine Re(0) complex see: (a) Wilgocki, M.; Szymanska, Buzar, T.; Jaroszewski, M.; Ziolkowski, J. J. in *Molecular Electrochemistry of Inorganic Bioinorganic and Organometallic Compounds*; Pombeiro, A. J. L., McCleverty, J. A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993; p 573. (b) Crocker, L. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 405.

(40) Kubiak, C. P.; Ratliff, K. S. *Isr. J. Chem.* **1991**, *31*, 3.

(41) (a) Reinhardt, R.; Fees, J.; Klein, A.; Sieger, M.; Kaim, W. In *Wasserstoff als Energieträger* (*Hydrogen As Energy Carrier*); VDI-Verlag: Düsseldorf, Germany, 1994; p 133. (b) See also: Kaim, W.; Reinhardt, R.; Sieger, M. *Inorg. Chem.* **1994**, *33*, 4453.