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Spectroelectrochemical (IR,UV/VIS) Determination of the Reduction Pathways for a Series of $[\text{Re}(\text{CO})\text{C}_3(\alpha\text{-diimine})\text{LE}']\text{E}^0\text{E}^+/ \text{E}^+$ ($\text{LE}'=\text{Halide}$, Otf , THF , MeCN , $n\text{-PrCN}$, $\text{PPhC}_3\text{C}'\text{P}(\text{OMe})\text{C}_3$) Complexes

Stor, G.J.; Hartl, F.; van Outersterp, J.W.M.; Stufkens, D.J.

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Spectroelectrochemical (IR, UV/Vis) Determination of the Reduction Pathways for a Series of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]^{0/+}$ ($\text{L}' = \text{Halide}, \text{Otf}^-, \text{THF}, \text{MeCN}, n\text{-PrCN}, \text{PPh}_3, \text{P}(\text{OMe})_3$) Complexes

G. J. Stor, F. Hartl,* J. W. M. van Outersterp, and D. J. Stufkens

Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received April 14, 1994*

The reduction pathways were investigated for a series of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]^{0/+}$ ($\text{L}' = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{Otf}^-, \text{THF}, \text{MeCN}, n\text{-PrCN}, \text{PPh}_3, \text{P}(\text{OMe})_3$; $\alpha\text{-diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{dapa}, \text{dpp}, \text{abpy}$) complexes. The individual one-electron reduction steps were studied mainly in THF, by a combination of cyclic voltammetry and in situ FTIR and UV/vis spectroscopy. The stability of the reduced $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]^{-/}$ complexes depends on the ability of the $\alpha\text{-diimine}$ radical ligand to accommodate the unpaired electron in its lowest empty π^* orbital, which increases in the order $\text{bpy} < i\text{-Pr-PyCa} < \text{dapa} < \text{dpp} < \text{abpy}$. The higher the energy of this π^* orbital, the more pronounced is the donor character of the $\alpha\text{-diimine}$ radical. Concomitant polarization of the radical complex and increased electron density within the $\text{Re}-(\alpha\text{-diimine})$ chelate ring labilize the $\text{Re}-\text{L}'$ bond and may cause dissociation of L' and dimerization of the Re radicals, or substitution of L' by a better π acceptor. The kinetic stability of the $\text{Re}-\text{L}'$ bond increases in the order $\text{halide} \ll \text{THF} < \text{PPh}_3, n\text{-PrCN} < \text{P}(\text{OMe})_3$. The labilizing effect of the strong donating power of the reduced $\alpha\text{-diimine}$ ligand on the $\text{Re}-\text{L}'$ bond becomes much more apparent upon the second one-electron reduction step. For $\alpha\text{-diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{dpp}$, the products of the first one-electron reduction were converted in this step into the five-coordinated anionic $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})]^-$ complexes, in which the π -electron density is largely delocalized over the $\text{Re}-(\alpha\text{-diimine})$ chelate bond, as indicated by their low $\nu(\text{CO})$ frequencies and average $\text{C}\equiv\text{O}$ force constants. For $\alpha\text{-diimine} = \text{dapa}$, the anionic $[\text{Re}(\text{CO})_3(N,N,(N)\text{-dapa})]^-$ species was produced, in which the third imine nitrogen atom interacts only weakly with the Re center. Importantly, for $\text{L}' = \text{P}(\text{OMe})_3$, the strongest π acceptor employed, the stable six-coordinated $[\text{Re}(\text{CO})_3(N,N\text{-dapa})(\text{P}(\text{OMe})_3)]^-$ anion was formed. The only stable six-coordinated $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]^-$ anions with $\text{L}' = \text{THF}$ or PPh_3 in the axial position were obtained for $\alpha\text{-diimine} = \text{abpy}$. The abpy ligand is a strong π acceptor due to its very low-lying π^* LUMO of the azo bond character. In this case, even a third one-electron reduction step was observed, which is probably more localized on the aromatic rings of abpy and converted the abpy ligand into a strong donor. As a result, the interaction of the ligand $\text{L}' = \text{THF}, \text{PPh}_3$ with the Re center in the dianionic product $\{[\text{Re}(\text{CO})_3(\text{abpy})]^{2-} \cdots \text{L}'\}$ is very weak.

Introduction

Complexes of the type $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]^{0/+}$, in which L' is a halide, bridging ligand, organic donor/acceptor, nitrogen donor or some other monodentate ligand, have been the subject of a large number of studies. In large part, this permanently growing interest stems from the ability of these complexes and their reduced forms to act as efficient sensitizers for energy and electron transfer processes,¹ and as catalysts in the selective reduction of CO_2 .² Thus, the complexes were successfully applied in the photochemical^{2a,c,e,h,j,m} and electrochemical^{2b,d,h,i,k,l,m,n} conversion of CO_2 into CO . In order to elucidate the role of these complexes as electrocatalysts in C_1 chemistry, most fundamental studies have mainly been confined to cyclic voltammetry^{2d,f,k} 3b-d

and ESR spectroscopy.^{3a,c,d} It has been established that the one-electron reduction of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]$ (L'

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Scheme 1

= halide) is exclusively localized on the α -diimine ligand, while in the subsequent one-electron reduction the Re center might also be involved. For $[\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}]$, a full description of the reduction pathways has been proposed,^{2f,k} which is mainly based on the data obtained by cyclic voltammetry. Quite recently, an analogous reaction sequence for $[\text{Re}(\text{CO})_3(\text{dmbpy})\text{Cl}]$ (dmbpy = 4,4'-dimethyl-2,2'-bipyridine) has been reported by Christensen et al.⁴ They followed for the first time the redox behavior of $[\text{Re}(\text{CO})_3(\text{dmbpy})\text{Cl}]$ by means of in situ FTIR reflection spectroscopy. In this way they were able to identify all reduction intermediates and products involved, as summarized in Scheme 1. The results obtained from these studies have clearly shown that the one-electron reduction of the bpy or dmbpy ligand in $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']$ results in the fast dissociation of the halide ligand L' .

Vogler et al.^{3d} have demonstrated for another series of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']$ ($\text{L}' = \text{Cl}^-, \text{Br}^-$) complexes that the labilization of the halide ligand upon the one-electron reduction, as studied by cyclic voltammetry and in situ ESR spectroscopy, depends strongly on the π -acceptor properties of the α -diimine ligand and the character of the halide ligand itself. Thus, in the $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']$ radical complexes, Br^- was more readily replaced by donor-solvent molecules (THF, MeCN) or by PPh_3 than Cl^- . In addition, the rate of this substitution reaction appeared to decrease significantly with increasing π -acceptor ability of the α -diimine ligand.

In this paper, we report electrochemical data for a representative series of complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']^{0/+}$ ($\text{L}' = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{Otf}^-$, donor solvent molecule, PR_3 ; α -diimine = 2,2'-bipyridine (bpy), pyridine-2-carbaldehyde *N*-isopropylimine (*i*-Pr-PyCa), 2,6-diacetylpyridine bis(anil) (dapa), 2,3-di(2-pyridyl)pyrazine (dpp), azo-2,2'-bipyridine (abpy)). These complexes were carefully chosen with the aim to vary systematically the influence of both the α -diimine and L' ligands on the reduction routes, and to investigate trends in the stability and the spectroscopic properties of the reduction products. The individual one-electron reduction steps and the following homogeneous reactions were

Figure 1. Structures of the α -diimine ligands and the general molecular geometry of the $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']^{0/+}$ complexes.

studied by conventional cyclic voltammetry and, for the spectroscopic characterization, by FTIR and UV/vis spectroelectrochemistry, performed in air-tight optically transparent thin-layer electrochemical (OTTLE) cells. The complexes studied are $[\text{Re}(\text{CO})_3(\text{bpy})\text{L}']^{0/+}$ ($\text{L}' = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{Otf}^-$, THF, PPh_3), $[\text{Re}(\text{CO})_3(\text{i-Pr-PyCa})\text{L}']^{0/+}$ ($\text{L}' = \text{Br}^-, \text{Otf}^-$, THF, *n*-PrCN, PPh_3), $[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]$, $[\text{Re}(\text{CO})_3(\text{abpy})\text{L}']^{0/+}$ ($\text{L}' = \text{Br}^-, \text{Otf}^-$, THF, PPh_3), and $[\text{Re}(\text{CO})_3(\text{N,N-dapa})\text{L}']^{0/+}$ ($\text{L}' = \text{Br}^-, \text{Otf}^-$, THF, MeCN, *n*-PrCN, PPh_3 , $\text{P}(\text{OMe})_3$). The structures of the α -diimine ligands and the complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']^{0/+}$ are schematically depicted in Figure 1.

Experimental Section

Materials and Preparations. Tetrahydrofuran (THF, Janssen) and acetonitrile (MeCN, Janssen) were distilled from

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Scheme 2

Scheme 3

a Na/benzophenone mixture and from P_2O_5 , respectively, under a nitrogen atmosphere. Butyronitrile ($n\text{-PrCN}$, Aldrich) was distilled from CaH_2 prior to use. The supporting electrolyte Bu_4NPF_6 (Fluka) was dried overnight under vacuum at 80°C . $\text{P}(\text{OMe})_3$ was distilled under vacuum from CaH_2 . Ferrocene (Fc) (BDH), bpy (Merck), dpp, PPh_3 , and Ag^+Otf^- ($\text{Otf}^- = \text{CF}_3\text{SO}_3^-$) (all Aldrich) were used as received.

The ligands $i\text{-Pr-PyCa}$,⁵ dapa,⁶ and abpy⁷ were synthesized according to literature procedures. The $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{-(halide)}]$ complexes ($\alpha\text{-diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{dapa}$) were prepared as previously described, with the modification that the reactions were performed by refluxing the components in toluene for 3 h. The synthesis of the $[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]$ complex

was performed following reported methods.¹⁰ For the synthesis of $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]$ the same procedure was followed as for the dinuclear $\{[\text{Re}(\text{CO})_3\text{Br}]_2(\mu\text{-abpy})\}$ species, except that a molar ratio $[\text{Re}(\text{CO})_3\text{Br}]/\text{abpy}$ of 1:3 was used in order to favor the formation of the mononuclear species. All the $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{halide})]$ complexes were purified by column chromatography on Silica 60, activated by heating overnight under vacuum at 150°C , with gradient elution of $n\text{-hexane}/\text{THF}$. The $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{Otf})]$ complexes were synthesized according to literature procedures,^{2c} except that Ag^+Otf^- instead of H^+Otf^- was used as a reactant. All electrochemical and spectroelectrochemical samples were degassed by several freeze-pump-thaw cycles and handled carefully under a nitrogen atmosphere.

Spectroscopic Measurements and Instrumentation.

IR spectra were measured on a Bio-Rad FTS-7 FTIR spectrometer (five scans, resolution 2 cm^{-1}). Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 5 UV/vis spectrophotometer, equipped with a 3600 data station. For IR and UV/vis spectroelectrochemical experiments at room

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Table 1. CO-Stretching Frequencies of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]$ ($\text{L} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{Otf}^-$; $\alpha\text{-Diimine} = \text{bpy}, i\text{-Pr-PyCa}$) and Their Reduction Products in THF, unless Stated Otherwise

complex	$\nu(\text{CO})$ (cm^{-1})	k_{av} (Nm^{-1})
$[\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}]$	2019 s, 1917 s, 1895 s	1527
$[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]$	2019 s, 1919 s, 1895 s	1528
$[\text{Re}(\text{CO})_3(\text{bpy})\text{I}]$	2020 s, 1921 s, 1900 s	1532
$[\text{Re}(\text{CO})_3(\text{bpy})(\text{Otf})]$	2034 s, 1930 s, 1914 s	1551
$[\text{Re}(\text{CO})_3(\text{bpy})(\text{THF})]^+$	2019 s, 1917 s, 1894 s	1526
$[\text{Re}(\text{CO})_3(\text{bpy})(\text{PPh}_3)]^+$	2037 s, 1950 s, 1922 s	1568
$[\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}]^-$	1996 s, 1883 s, 1868 s	1483
$[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]^-$	1997 s, 1888 s, 1867 s	1486
$[\text{Re}(\text{CO})_3(\text{bpy})\text{I}]^-$	1995 s, 1889 s, 1866 s	1485
$[\text{Re}(\text{CO})_3(\text{bpy})(\text{PPh}_3)]^-$	2015 s, 1919 s, 1892 s	1524
$[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$	1988 s, 1951 s, 1887 s 1859 s	
$[\text{Re}(\text{CO})_3(\text{bpy})]^-$	1947 m, 1843 s, br	1425
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})\text{Br}]$	2020 s, 1919 s, 1897 s	1529
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{Otf})]$	2034 s, 1934 s, 1912 s	1552
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{THF})]^+$	2020 s, 1919 s, 1896 s	1529
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(n\text{-PrCN})]^+{}^b$	2036 s, 1930 s, br	1561
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{PPh}_3)]^+$	2037 s, 1951 s, 1923 s	1569
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})\text{Br}]^-$	1994 s, 1875 s, 1849 s	1469
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{THF})]^-$	1995 s, 1875 s, 1851 s	1470
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(n\text{-PrCN})]^-{}^b$	2005 s, 1886 s, br	1499
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{PPh}_3)]^-$	2011 s, 1914 s, 1887 s	1517
$[\text{Re}_2(\text{CO})_6(i\text{-Pr-PyCa})_2]^c$	1984 s	
$[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})_2]^a$	2014 s, 1993 s, 1907 m, 1890 vs, 1871 s	
$[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})_2]^{a,b}$	2017 s, 1994 s, 1913 m, 1893 vs, 1874 sh	
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})]^-$	1948 m, 1840 s, br	1422
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})]^-{}^b$	1946 m, 1845 s, br	1426
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(n\text{-PrCN})]^-{}^{b,c}$	1980 m	

^a The imine-carbon atoms of the *i*-Pr-PyCa ligands are coupled. ^b In *n*-PrCN at room temperature. ^c Other $\nu(\text{CO})$ bands could not be observed.

temperature an OTTLE cell¹¹ was used, equipped with a Pt-minigrid working electrode (32 wires/cm). Spectroelectrochemistry at low temperature was performed in a homemade cryostated OTTLE cell, which has been described in detail elsewhere.¹² Either NaCl or CaF₂ windows were utilized for IR OTTLE measurements and CaF₂ or quartz windows were employed for UV/vis OTTLE measurements. The working electrode surroundings were carefully masked to avoid the spectral beam passing through the nonelectrolyzed solution. Cyclic voltammetry and controlled-potential electrolyses within the OTTLE cell were carried out by using a PAR Model 174 potentiostat. For all spectroelectrochemical samples, the concentrations of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]^{0/+}$ and Bu₄NPF₆ were 10⁻² M and 3 × 10⁻¹ M, respectively. Cyclic voltammograms were recorded under the following conditions: 10⁻³ M $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]^{0/+}$ in THF in the presence of 10⁻¹ M Bu₄NPF₆, Pt disk electrode of 0.8 mm² area. All potentials are reported with respect to the standard¹³ ferrocene/ferrocenium (Fc/Fc⁺) couple.

Results

IR Spectroelectrochemistry. All $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]^{0/+}$ complexes studied undergo two subsequent reduction steps which may be followed by secondary chemical reactions (see Schemes 2–6). Infrared spectra of the reduction products were investigated in the CO-stretching region, and the frequencies are summarized in Tables 1–3. Reduction of the carbonyl complexes will be accompanied by a lowering of the stretching frequen-

Table 2. CO-Stretching Frequencies of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]$ ($\text{L} = , \text{Br}^-, \text{Otf}^-$; $\alpha\text{-Diimine} = \text{dpp}, \text{abpy}$) and Their Reduction Products in THF

complex	$\nu(\text{CO})$ (cm^{-1})	k_{av} (Nm^{-1})
$[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]$	2023 s, 1924 s, 1903 s	1537
$[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]^-$	2000 s, 1891 s, 1875 s	1493
$[\text{Re}(\text{CO})_3(\text{dpp})(\text{THF})]^-$	2008 s, 1898 s, 1881 s	1504
$[\text{Re}(\text{CO})_3(\text{dpp})(\text{PPh}_3)]^-$	2014 s, 1922 s, 1896 s	1527
$[\text{Re}(\text{CO})_3(\text{dpp})]^-$	1960 m, 1855 s, br	1444
$[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]$	2028 s, 1943 s, 1917 s	1556
$[\text{Re}(\text{CO})_3(\text{abpy})(\text{Otf})]$	2039 s, 1953 s, 1928 s	1573
$[\text{Re}(\text{CO})_3(\text{abpy})(\text{THF})]^+$	2026 s, 1941 s, 1915 s	1553
$[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]^+$	2044 s, 1972 s, 1946 s	1596
$[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^-$	2004 s, 1900 s, 1871 s	1498
$[\text{Re}(\text{CO})_3(\text{abpy})(\text{THF})]^-$	2017 s, 1915 s, 1893 s	1524
$[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]^-$	2019 s, 1934 s, 1896 s	1536
$[\text{Re}(\text{CO})_3(\text{abpy})(\text{THF})]^-$	1984 s, 1880 s, 1854 s	1468
$[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]^-$	1991 s, 1891 s, 1860 s	1481
$\{[\text{Re}(\text{CO})_3(\text{abpy})]^{2-\cdots}\text{THF}\}$	1966 s, 1845 s, 1807 s	1418
$\{[\text{Re}(\text{CO})_3(\text{abpy})]^{2-\cdots}\text{PPh}_3\}$	1970 s, 1840 s, 1813 s	1421

cies and force constants of the CO ligands in the products. In particular, the changes in force constants along the redox series are good indicators of the changing donor/acceptor character of the α -diimine ligand. The CO-stretching vibrations of the mononuclear tricarbonyl complexes, having C_s symmetry, are described by four C≡O force constants, viz. k_{ax} , k_{eq} , $k_{\text{ax,eq}}$, and $k_{\text{eq,eq}}$. These force field parameters can only be calculated, using the Cotton-Kraihanzel Energy Factored Force Fields method,^{14a,b} when the frequencies of the ¹³CO-enriched positional isotopomers are also known.^{14c} This allows then the correct assignment of the two low-frequency $\nu(\text{CO})$ bands to the A' and (A')₂ normal vibrational modes for all members of a redox series. The empirical method by Timney^{14d} requires knowledge of the geometry of the complexes which may vary appreciably, see e.g. the formation of pentacoordinated species $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})]^-$ (vide infra). Therefore, only the average C≡O force constants k_{av} ^{14e} were calculated according to eq 1 (see Tables 1–3) and employed in a qualitative discussion of the electronic effects:

$$k_{\text{av}} = 4.0383 \times 10^{-4} \sum_i g_i \nu_i^2 / \sum_i g_i \quad (1)$$

where g_i is the degeneracy of the *i*th CO-stretching mode, of frequency ν_i (cm^{-1}).

A lowering of k_{av} as a result of the reduction means that the Re→CO π -back-bonding increased. This clearly indicates that the added electrons are at least partly delocalized within the Re-(α -diimine) chelate ring, which in turn increases the electron density on the Re center. The delocalization plays an important role for the stability and composition of the reduction products and depends considerably on the varying π -acceptor/ σ , π -donor properties of the α -diimine ligands under study (vide infra).

One-Electron Reduction of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]$ ($\alpha\text{-Diimine} = \text{bpy}, \text{L}' = \text{Cl}^-, \text{Br}^-, \text{I}^-$; $\alpha\text{-Diimine} = i\text{-Pr-PyCa}, \text{dpp}, \text{abpy}, \text{L}' = \text{Br}^-$) in THF. One-electron reduction of $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]$ in THF/Bu₄NPF₆

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Figure 2. Structure of the C–C-coupled dimer $[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})_2]$.¹⁶

at 293 K afforded the radical anion $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]^{\cdot-}$ ($\nu(\text{CO})$ at 1997, 1888, and 1867 cm^{-1})⁴ only in very low yield. The formation of the closely related radical $[\text{Re}(\text{CO})_3(\text{bpy})(\text{THF})]^\cdot$ can be excluded here since this radical appeared to be very unstable when formed by one-electron reduction of $[\text{Re}(\text{CO})_3(\text{bpy})(\text{THF})]^+$ (vide infra). The second, major product formed upon reduction of $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]$ was identified as the metal–metal-bonded dimer $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$ ($\nu(\text{CO})$ at 1988, 1951, 1887, and 1859 cm^{-1} ; UV/vis $\lambda_{\text{max}} = 805, 600, 470\text{ nm}$), in accordance with literature data.^{1f,h,i,15} The concentration of $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]^{\cdot-}$ gradually decreased in the course of the electrolysis. Most probably, the radical anion lost Br^- and transformed into $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$.

One-electron reduction of the complexes $[\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}]$ and $[\text{Re}(\text{CO})_3(\text{bpy})\text{I}]$ also gave $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$ as the main product, together with a small amount of $[\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}]^{\cdot-}$ ($\nu(\text{CO})$ at 1996, 1883, and 1868 cm^{-1}) and $[\text{Re}(\text{CO})_3(\text{bpy})\text{I}]^{\cdot-}$ ($\nu(\text{CO})$ at 1995, 1889, and 1866 cm^{-1}), respectively. From the radical anions $[\text{Re}(\text{CO})_3(\text{bpy})\text{L}]^{\cdot-}$, the Cl derivative appeared to be most stable and could be generated at much higher concentration than the corresponding Br and I complexes under identical conditions. A similar trend has been observed for the closely related $[\text{Re}(\text{CO})_3(\text{dab})\text{L}]^{\cdot-}$ ($\text{L}' = \text{Cl}^-, \text{Br}^-$) species.^{3d}

One-electron reduction of $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})\text{Br}]$ in THF yielded both $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})\text{Br}]^{\cdot-}$ ($\nu(\text{CO})$ at 1994, 1875, and 1849 cm^{-1}) and the metal–metal-bonded dimer $[\text{Re}_2(\text{CO})_6(i\text{-Pr-PyCa})_2]$ ($\nu(\text{CO})$ at 1984 cm^{-1} , other bands obscured; UV/vis $\lambda_{\text{max}} = 785\text{ nm}$) only as minor products. Instead, a novel complex was obtained with $\nu(\text{CO})$ bands at 2014, 1993, 1907, 1890, and 1871 cm^{-1} . Quite recently, this product has been isolated and structurally characterized by X-ray diffraction.¹⁶ It appeared to be a C–C-coupled dimer containing two $\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})$ fragments and no Re–Re bond. The imine nitrogen atoms of the two $i\text{-Pr-PyCa}$ ligands have adopted a bridging coordination to the two Re centers and the imine carbon atoms of these two ligands are coupled (see Figure 2). The formation of this complex, which will be denoted as $[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})_2]$, most likely occurs by a radical coupling reaction. A detailed description of its structure will be given in a forthcoming article.¹⁶

One-electron reduction of $[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]$ in THF (Scheme 4) also led to the formation of the radical

anionic complex $[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]^{\cdot-}$, as evidenced by its CO-stretching frequencies at 2000, 1891, and 1875 cm^{-1} which closely resemble those of $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]^{\cdot-}$ (Table 1). However, contrary to the related bpy and $i\text{-Pr-PyCa}$ complexes, the radical anion did not easily lose Br^- and did not transform into the dimer $[\text{Re}_2(\text{CO})_6(\text{dpp})_2]$. Instead, $[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]^{\cdot-}$ slowly converted into a new, stable product with $\nu(\text{CO})$ frequencies at 2008, 1898, and 1881 cm^{-1} . These frequencies closely resemble those of the solvated radicals $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{THF})]^\cdot$ ($\alpha\text{-diimine} = i\text{-Pr-PyCa}, \text{abpy}$) (see Tables 1 and 2) and are therefore attributed to $[\text{Re}(\text{CO})_3(\text{dpp})(\text{THF})]^\cdot$.

In sharp contrast to the above-mentioned complexes, no dissociation of Br^- occurred upon one-electron reduction of $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]$ in THF (see Figure 3). The radical anionic product $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^{\cdot-}$ ($\nu(\text{CO})$ at 2004, 1900, and 1871 cm^{-1}) did not decompose at the applied reduction potential of the parent complex even 30 min after the reduction had been completed. It is thus the most stable member of the series of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{Br}]^{\cdot-}$ complexes under study.

All complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{Br}]$ appeared to be thermally stable in the presence of a 100-fold excess of PPh_3 . However, substitution of Br^- by the better π acceptor PPh_3 was observed upon the one-electron reduction of the parent complexes. The substitution was very fast for $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]^{\cdot-}$ since this radical anion was formed in the course of the electrolysis only as a minor product with a very weak $\nu(\text{CO})$ band at 1997 cm^{-1} (Table 1). The main product was identified as the radical $[\text{Re}(\text{CO})_3(\text{bpy})(\text{PPh}_3)]^\cdot$ ($\nu(\text{CO})$ at 2017, 1918, and 1894 cm^{-1}) by the close similarity of its $\nu(\text{CO})$ frequencies with those of $[\text{Mn}(\text{CO})_3(\text{bpy})(\text{P}(\text{nBu})_3)]^\cdot$ at 2012, 1923, and 1891 cm^{-1} .¹⁷ No dimer $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$ was detected in this case. This observation again illustrates that the Re–Br bond in the reduced complex $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]^{\cdot-}$ is strongly labilized. $[\text{Re}(\text{CO})_3(\text{bpy})(\text{PPh}_3)]^\cdot$ was reoxidized to give initially a product with $\nu(\text{CO})$ bands at 2037, 1950, and 1922 cm^{-1} , which are assigned to the cation $[\text{Re}(\text{CO})_3(\text{bpy})(\text{PPh}_3)]^+$.¹⁸ $[\text{Re}(\text{CO})_3(\text{bpy})(\text{PPh}_3)]^+$ reacted back thermally with Br^- , still present in the solution, to give the parent complex $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]$.

In contrast to this, the conversion of the initially generated radical anions $[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]^{\cdot-}$ and, in particular, $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^{\cdot-}$ into the radicals $[\text{Re}(\text{CO})_3(\text{dpp})(\text{PPh}_3)]^\cdot$ ($\nu(\text{CO})$ at 2014, 1922, and 1896 cm^{-1}) and $[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]^\cdot$ ($\nu(\text{CO})$ at 2019, 1934, and 1896 cm^{-1}) was a very slow process which required typically more than 10 min for its completion.

One-Electron Reduction of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]$ ($\alpha\text{-Diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{abpy}, \text{L}' = \text{Otf}^-$). One-electron reduction of the complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{Otf})]$ with the weakly coordinated Otf^- (CF_3SO_3^-) ligand was studied by IR spectroelectrochemistry with the aim to provide more evidence for correct assignment of the various reduction products obtained from the secondary chemical reactions of the radical anions $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{Br}]^{\cdot-}$ (vide supra). This strategy was particularly helpful in those cases where the

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Figure 3. IR (CO-stretching region) (A) and UV/vis (B) spectra of the products formed during the three-step one-electron reduction of [Re(CO)₃(abpy)Br] in THF: (—) [Re(CO)₃(abpy)Br]; (---) [Re(CO)₃(abpy)Br]⁻; (- · -) [Re(CO)₃(abpy)(THF)]⁻; (···) {[Re(CO)₃(abpy)]²⁻·THF}.

dissociation of the Br⁻ ligand was a slow process, or when the assignment of the ν(CO) bands was not straightforward due to near coincidence of the ν(CO)

frequencies for different compounds, such as [Re(CO)₃(bpy)Br]/[Re(CO)₃(bpy)(THF)]⁺ or [Re(CO)₃(*i*-PrPyCa)Br]⁻/[Re(CO)₃(*i*-Pr-PyCa)(THF)]⁻ (Table 1).

Figure 4. IR (CO-stretching region) (A) and UV/vis (B) spectral changes during two successive one-electron reductions of $[\text{Re}(\text{CO})_3(\text{bpy})(\text{Otf})]$ in THF: (1) $[\text{Re}(\text{CO})_3(\text{bpy})(\text{Otf})]$; (2) $[\text{Re}(\text{CO})_3(\text{bpy})(\text{THF})]^+$; (3) $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$; (4) $[\text{Re}(\text{CO})_3(\text{bpy})]^-$.

All complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{Otf})]$ ($\alpha\text{-diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{abpy}$) (Tables 1 and 2) were transformed already at the onset of the one-electron reduction in THF into the cationic complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{THF})]^+$ (see Figure 4A). Similarly, the cations $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{PPh}_3)]^+$ were obtained in the presence of a 100-fold excess of PPh_3 in THF. For example, the corresponding thermal substitution of Otf^- by THF or PPh_3 in the complex $[\text{Re}(\text{CO})_3(\text{bpy})(\text{Otf})]$ took several hours at ambient temperature. This electrocatalytic ligand substitution reaction was not further investigated and most likely occurs via the same mechanism as proposed by Kochi et al.¹⁹ for the related electrocatalytic substitution of MeCN in $[(\text{MeCp})\text{Mn}(\text{CO})_2(\text{MeCN})]$ by PR_3 or $\text{P}(\text{OR})_3$. In our case, the radical chain process is initiated by substitution of the labile Otf^- ligand in the reduced complex $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{Otf})]^-$ by either THF or PPh_3 to give the radicals $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]^\cdot$ ($\text{L}' = \text{THF}$ or PPh_3).

As follows from Table 7, both radicals can transfer the unpaired electron to parent $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{Otf})]$, by which process they are oxidized to the corresponding cations (the propagation step). The electrocatalytic reaction is terminated by one-electron oxidation of the radicals $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]^\cdot$ at the electrode potential applied. The latter, heterogeneous electron transfer at the electrode surface may significantly compete with the homogeneous electron transfer provided that both processes are outer-sphere electron transfers. Since this is likely the case, both, radical chain and electrode mediated,¹⁹ electrocatalytic mechanisms may operate.

One-electron reduction of the cations $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]^+$ ($\alpha\text{-diimine} = \text{bpy}$ (see Figure 4), $i\text{-Pr-PyCa}$, abpy ; $\text{L}' = \text{THF}$, PPh_3) at a lower electrode potential gave primarily the corresponding radicals $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]^\cdot$ (see Schemes 2, 3, and 5 and Tables 1 and 2). The radicals $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{PPh}_3)]^\cdot$ were formed as single, stable species. Contrary to this, stable

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radicals $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{THF})]^\cdot$ were obtained only for the abpy and dpp (see above, and Scheme 4) complexes. $[\text{Re}(\text{CO})_3(\text{bpy})(\text{THF})]^\cdot$ converted to the dimer $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$ as the only detectable product. $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{THF})]^\cdot$ was formed only in low yield, together with a very small amount of the metal-metal-bonded dimer $[\text{Re}_2(\text{CO})_6(i\text{-Pr-PyCa})_2]$. The C-C-coupled dimer $[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})_2]$ (Figure 2) was the main product in this case.

A different reaction sequence was observed for $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{Otf})]^\cdot$ in *n*-PrCN. The complex transformed thermally into a product with $\nu(\text{CO})$ bands at 2036 and 1930 (broad) cm^{-1} . The two lowest frequency $\nu(\text{CO})$ bands coincide. This effect has also been observed for several $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{MeCN})]^\cdot$ complexes.^{3d} This $\nu(\text{CO})$ pattern is a typical property of $[\text{Re}(\text{CO})_3(\text{N})_3]^+$ complexes, having three N-donor atoms trans to the carbonyls (a local C_{3v} symmetry). Therefore, we identify the product as $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(n\text{-PrCN})]^\cdot$. One-electron reduction of this cation afforded two products in comparable concentrations: the C-C-coupled dimer $[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})_2]$ and a second complex with $\nu(\text{CO})$ bands at 2005 and 1886 (broad) cm^{-1} . Again on the basis of the broadness of the 1886 cm^{-1} band,^{3d} the latter frequencies are assigned to the $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(n\text{-PrCN})]^\cdot$ radical. Both processes, the thermal conversion of $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{Otf})]^\cdot$ into $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(n\text{-PrCN})]^\cdot$ and the formation of the solvent-stabilized radical $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(n\text{-PrCN})]^\cdot$, show that *n*-PrCN coordinates more strongly to the Re center than THF.

In Situ Electrochemical Generation of Doubly Reduced Anions $[\text{Re}(\text{CO})_3(\alpha\text{-Diimine})]^{2-}$ ($\alpha\text{-Diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{dpp}$) and $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{-L}]^{2-}$ ($\alpha\text{-Diimine} = i\text{-Pr-PyCa}, \text{L}' = n\text{-PrCN}$; $\alpha\text{-Diimine} = \text{abpy}, \text{L}' = \text{THF}, \text{PPh}_3$). All singly reduced $\text{Re}(\alpha\text{-diimine})$ complexes, described in the preceding text, could be reduced in a subsequent one-electron, $\alpha\text{-diimine}$ -localized step. The composition of the doubly reduced species was mainly dependent on the particular $\alpha\text{-diimine}$ ligand used (see schemes 2–5 and Figures 3 and 4).

Reduction of $[\text{Re}(\text{CO})_3(\text{bpy})\text{L}']^\cdot$ ($\text{L}' = \text{Cl}^-, \text{Br}^-, \text{I}^-$), stabilized by an excess of L' in the solution, of the metal-metal-bonded dimer $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$, and of the radical $[\text{Re}(\text{CO})_3(\text{bpy})(\text{PPh}_3)]^\cdot$ produced the same compound possessing $\nu(\text{CO})$ bands at 1947 and 1843 (broad) cm^{-1} (see Figure 4A). These frequencies are assigned to the five-coordinated anionic complex $[\text{Re}(\text{CO})_3(\text{bpy})]^{2-}$, in accordance with previous results obtained by cyclic voltammetry,^{2f,k} with the results of Christensen et al.,⁴ and with its invariable $\nu(\text{CO})$ frequencies, regardless the composition of the parent complexes. Similarly, $[\text{Re}(\text{CO})_3(\text{dpp})]^\cdot$ ($\nu(\text{CO})$ at 1960 and 1855 (broad) cm^{-1}) was obtained by one-electron reduction of both $[\text{Re}(\text{CO})_3(\text{dpp})(\text{THF})]^\cdot$ and $[\text{Re}(\text{CO})_3(\text{dpp})(\text{PPh}_3)]^\cdot$. It should be noted that all reductions were fully chemically reversible. Reoxidation of $[\text{Re}(\text{CO})_3(\text{bpy})]^{2-}$ in THF in the presence of 1 equiv of Br^- led both to $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$ and a small amount of $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]^\cdot$. This observation indicates existence of an equilibrium between the two products (see Scheme 2).

The closely related anion $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})]^{2-}$ ($\nu(\text{CO})$ at 1948 and 1840 (broad) cm^{-1}) was formed in THF by reduction of $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})\text{Br}]^\cdot$, $[\text{Re}(\text{CO})_3(i\text{-Pr-}$

$\text{PyCa})(\text{THF})]^\cdot$ (both generated in low concentration in THF, see above) and the stable radical $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{PPh}_3)]^\cdot$, and of the dimers $[\text{Re}_2(\text{CO})_6(i\text{-Pr-PyCa})_2]$ and $[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})]$. Only in *n*-PrCN, the reduction of $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(n\text{-PrCN})]^\cdot$, present in equilibrium with $[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})]$ (see above), afforded a small amount of the six-coordinated anion $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(n\text{-PrCN})]^{2-}$ having a weak $\nu(\text{CO})$ band at 1981 cm^{-1} . The lower $\nu(\text{CO})$ frequencies of this anion were obscured by those of dominant $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})]^{2-}$ ($\nu(\text{CO})$ at 1946 and 1845 (broad) cm^{-1}). Nevertheless, the assignment of the 1981 cm^{-1} band to $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(n\text{-PrCN})]^{2-}$ is strongly supported by the IR spectra of $[\text{Re}(\text{CO})_3(\text{N,N-dapa})(n\text{-PrCN})]^{2-}$ (see below, Table 3) and $[\text{Re}(\text{CO})_3(\text{bpy})(n\text{-PrCN})]^{2-}$ ($\nu(\text{CO})$ at 1980, 1861, and 1851 cm^{-1}). The latter six-coordinated anion was recently generated²⁰ in high yield in *n*-PrCN at 213 K.

A remarkable difference in behavior upon reduction was observed for the radical complexes containing the abpy ligand. In THF, both stable radicals $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^\cdot$ and $[\text{Re}(\text{CO})_3(\text{abpy})(\text{THF})]^\cdot$ were converted in separate experiments into the same product with three distinct $\nu(\text{CO})$ bands at 1984, 1880, and 1854 cm^{-1} (see Scheme 5 and Figure 3A). In contrast, $[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]^\cdot$ was reduced to give a different species which exhibited $\nu(\text{CO})$ vibrations at 1991, 1891, and 1860 cm^{-1} . The appearance of three new $\nu(\text{CO})$ bands indicates that the doubly reduced complexes have retained a six-coordinated geometry since the related six-coordinated complexes $[\text{Re}(\text{CO})_3(\text{DBCat})\text{L}']^{2-}$ ($\text{L}' = \text{PPh}_3$)²¹ and adducts $[\text{Mn}(\text{CO})_3(\text{DBCat})]^\cdot\text{-L}'$ ($\text{DBCat} = 3,5\text{-di-}t\text{-tert-butylcatechol}$, $\text{L}' = \text{pyridine}, \text{PPh}_3, \text{P}(\text{cHex})_3$)²² also exhibit three well-separated $\nu(\text{CO})$ bands. Up to now, only five-coordinated anions such as $[\text{Mn}(\text{CO})_3(\text{DBCat})]^{2-}$,²² $[\text{W}(\text{CO})_3(\text{DBCat})]^{2-}$,²³ $[\text{Mn}(\text{CO})_3(\text{bpy})]^{2-}$,¹⁷ and $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})]^{2-}$ ($\alpha\text{-diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{dpp}$) (see Tables 1 and 2) appeared to be characterized by only two $\nu(\text{CO})$ bands. The doubly reduced products are therefore assigned as $[\text{Re}(\text{CO})_3(\text{abpy})(\text{THF})]^{2-}$ and $[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]^{2-}$, respectively.

Contrary to the other complexes, both $[\text{Re}(\text{CO})_3(\text{abpy})(\text{THF})]^{2-}$ and $[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]^{2-}$ could even be reduced in a third one-electron step. The resulting products showed three well-separated CO-stretching vibrations of equal intensities at 1966, 1845, and 1807 cm^{-1} , and at 1970, 1840, and 1813 cm^{-1} , respectively. The small difference between the corresponding average CO force constants k_{av} (see Table 2) implies that the sixth ligand $\text{L}' = \text{THF}, \text{PPh}_3$ only weakly interacts with the Re center. Hence, both dianionic complexes are formulated as $\{[\text{Re}(\text{CO})_3(\text{abpy})]^{2-} \cdots \text{L}'\}$.

Reduction of $[\text{Re}(\text{CO})_3(\text{N,N-dapa})\text{L}']^{2-}$ ($\text{L}' = \text{Br}^-, \text{Otf}^-$). In both starting complexes, the dapa ligand is bidentately coordinated to the Re center via the pyridine nitrogen atom and one of the imine nitrogen atoms, as

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Scheme 5

evidenced by the ^1H NMR spectra.^{9,24e} Contrary to the other complexes discussed so far, this ligand may, however, use its nitrogen-donor sidearm to adopt a tridentate coordination. In order to find out if this property plays an important role in the redox chemistry we studied the reduction pathways of $[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})\text{L}']$ in detail.

When $[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{Otf})]$ was dissolved in THF, a slow thermal reaction occurred to give a product with CO-stretching vibrations at 2022, 1925, and 1900 cm^{-1} . As such a reaction was not observed for $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{Otf})]$ (see above), these frequencies are attributed to the six-coordinated $[\text{Re}(\text{CO})_3(\text{N},\text{N},\text{N}\text{-dapa})]^+$ complex, in which the Otf^- anion has been substituted by the third nitrogen atom of the dapa ligand. This indicates that this donor atom coordinates more strongly than THF. All $[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{Otf})]$, not yet thermally transformed into $[\text{Re}(\text{CO})_3(\text{N},\text{N},\text{N}\text{-dapa})]^+$, reacted to give the latter product in 100% yield prior to the onset of the first one-electron reduction step. The thermal lability of $[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{Otf})]$ became evident when the complex was dissolved in THF/100-fold excess of PPh_3 , or in MeCN or *n*-PrCN. In the former case, a mixture of $[\text{Re}(\text{CO})_3(\text{N},\text{N},\text{N}\text{-dapa})]^+$ and $[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{PPh}_3)]^+$ was obtained, whereas in the latter case, $[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})\text{L}']^+$ ($\text{L}' = \text{MeCN}$ or *n*-PrCN) was exclusively formed (see Table 3 for the corresponding $\nu(\text{CO})$ frequencies). These thermal reactions clearly illustrate that there is a competition between PPh_3 and the third nitrogen atom of the dapa ligand regarding their coordination to Re, and that MeCN and *n*-PrCN coordinate more firmly than PPh_3 in the cationic

Table 3. CO-Stretching Frequencies of $[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})\text{L}']$ ($\text{L}' = \text{Br}^-, \text{Otf}^-$) and Their Reduction Products in THF, unless Stated Otherwise

complex	$\nu(\text{CO})$ (cm^{-1})	k_{av} (Nm^{-1})
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})\text{Br}]$	2022 s, 1924 s, 1901 s	1535
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{Otf})]$	2033 s, 1935 s, 1916 s	1555
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{MeCN})]^+{}^a$	2037 s, 1934 s, br	1566
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(n\text{-PrCN})]^+{}^b$	2038 s, 1936 s, br	1568
$[\text{Re}(\text{CO})_3(\text{N},\text{N},\text{N}\text{-dapa})]^+$	2022 s, 1925 s, 1900 s	1535
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{PPh}_3)]^+$	2036 s, 1949 s, 1927 s	1569
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{P}(\text{OMe})_3)]^+$	2044 s, 1963 s, 1929 s	1582
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{MeCN})]^+{}^a$	2009 s, 1899 s, br	1514
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(n\text{-PrCN})]^+{}^b$	2012 s, 1901 s, br	1518
$[\text{Re}(\text{CO})_3(\text{N},\text{N},\text{N}\text{-dapa})]^\bullet$	2000 s, 1887 s, 1860 s	1483
$[\text{Re}(\text{CO})_3(\text{N},\text{N},\text{N}\text{-dapa})]^\bullet{}^a$	1998 s, 1886 s, 1852 s	1478
$[\text{Re}(\text{CO})_3(\text{N},\text{N},\text{N}\text{-dapa})]^\bullet{}^b$	2000 s, 1891 s, 1853 s	1481
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{PPh}_3)]^\bullet$	1964 s, 1856 s, 1840 s	1439
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{P}(\text{OMe})_3)]^\bullet$	2011 s, 1914 s, 1891 s	1519
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{P}(\text{OMe})_3)]^\bullet$	2020 s, 1929 s, 1898 s	1535
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{P}(\text{OMe})_3)]^\bullet$	1940 s, 1862 s	1460
$[\text{Re}(\text{CO})_3(\text{N},\text{N},\text{N}\text{-dapa})]^\bullet$	1940 s, 1856 s, 1840 s	1439
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{MeCN})]^\bullet{}^a$	1983 s, 1865 s, 1842 s	1454
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(n\text{-PrCN})]^\bullet{}^b$	1980 s, 1856 s, 1842 s	1448
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(n\text{-PrCN})]^\bullet{}^c$	1980 s, 1865 s, 1843 s	1453
$[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{P}(\text{OMe})_3)]^\bullet$	1997 s, 1892 s, 1872 s	1490

^a In MeCN at 243 K. ^b In *n*-PrCN at 233 K. ^c In *n*-PrCN at room temperature.

complexes when used as solvents. In accordance, no $[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})(\text{PPh}_3)]^+$ appeared in MeCN or *n*-PrCN.

Similar competitive substitution reactions took place even during the one-electron reduction of the aforementioned dapa complexes (see Scheme 6). Upon passing the one-electron reduction step in THF, $[\text{Re}(\text{CO})_3(\text{N},\text{N}\text{-dapa})]^\bullet$ was smoothly converted into a product

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Scheme 6

with CO-stretching vibrations at 2000, 1887, and 1860 cm^{-1} . These frequencies can reasonably be assigned to the radical $[\text{Re}(\text{CO})_3(\text{N},\text{N},\text{N-dapa})]$, as coordination of THF has been found to be too weak (see above) to compete significantly. It should be noted that the intensity pattern of the $\nu(\text{CO})$ bands of both $[\text{Re}(\text{CO})_3(\text{N},\text{N},\text{N-dapa})]^+$ and $[\text{Re}(\text{CO})_3(\text{N},\text{N},\text{N-dapa})]^\bullet$ (see Table 3) rules out their meridional geometry with in-plane coordinated dapa.^{16,24,25}

One-electron reduction of $[\text{Re}(\text{CO})_3(\text{N},\text{N-dapa})\text{L}']^+$ ($\text{L}' = \text{MeCN}$ or $n\text{-PrCN}$) initially afforded the corresponding radicals $[\text{Re}(\text{CO})_3(\text{N},\text{N-dapa})\text{L}']^\bullet$ with typically coincident lower $\nu(\text{CO})$ frequencies (see Table 3). However, in contrast to the cations $[\text{Re}(\text{CO})_3(\text{N},\text{N-dapa})\text{L}']^+$ ($\text{L}' = \text{MeCN}$ or $n\text{-PrCN}$), the radicals appeared to be thermally more labile, as they slowly transformed to $[\text{Re}(\text{CO})_3(\text{N},\text{N},\text{N-dapa})]$, even when the temperature was decreased to 243 K (in MeCN) or to 223 K (in $n\text{-PrCN}$). In the presence of PPh_3 , the radical $[\text{Re}(\text{CO})_3(\text{N},\text{N-dapa})\text{L}']^\bullet$ was obtained as the major product besides a

small amount of $[\text{Re}(\text{CO})_3(\text{N},\text{N},\text{N-dapa})]$. These results clearly indicate that, in particular, coordination of a better π -acceptor is more important for the stability of the radicals, than for that of the parent cationic complexes.

Exactly the same conclusion can be drawn for the complexes $[\text{Re}(\text{CO})_3(\text{N},\text{N-dapa})\text{Br}]^{0/+}$ and $[\text{Re}(\text{CO})_3(\text{N},\text{N-dapa})(\text{P}(\text{OMe})_3)]^{0/+}$ (see Scheme 6). The only exception to the reactivity pattern of the tricarbonyl complexes, as outlined above, was an occurrence of a CO-substitution reaction for the radical $[\text{Re}(\text{CO})_3(\text{N},\text{N-dapa})(\text{P}(\text{OMe})_3)]^\bullet$ in the presence of excess $\text{P}(\text{OMe})_3$ which afforded a bis(carbonyl) product with two intense $\nu(\text{CO})$ bands at 1940 and 1862 cm^{-1} . As such a CO substitution was not observed in the presence of excess PPh_3 , it is concluded that $[\text{Re}(\text{CO})_2(\text{N},\text{N-dapa})(\text{P}(\text{OMe})_3)_2]^\bullet$ had been formed.

In a subsequent one-electron reduction step, $[\text{Re}(\text{CO})_2(\text{N},\text{N-dapa})(\text{P}(\text{OMe})_3)_2]^\bullet$ was converted into a tricarbonyl complex with $\nu(\text{CO})$ bands at 1997, 1892, and 1872 cm^{-1} .

Table 4. Absorption Maxima in the Visible Region of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]$ ($\text{L}' = \text{Cl}^-$, Br^- , I^- , Otf^- ; $\alpha\text{-Diimine} = \text{bpy}$, $i\text{-Pr-PyCa}$) and Their Reduction Products in THF

complex	λ_{max} (nm)
$[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]$	385
$[\text{Re}(\text{CO})_3(\text{bpy})(\text{Otf})]$	355
$[\text{Re}(\text{CO})_3(\text{bpy})(\text{THF})]^+$	385
$[\text{Re}(\text{CO})_3(\text{bpy})(\text{PPh}_3)]^+$	365, 330
$[\text{Re}(\text{CO})_3(\text{bpy})(\text{PPh}_3)]^-$	500, 390
$[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$	805, 600, 470
$[\text{Re}(\text{CO})_3(\text{bpy})]^-$	750 sh, 680 sh, 630 sh, 560
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})\text{Br}]$	410
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{Otf})]$	365, 270
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{THF})]^+$	380
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{PPh}_3)]^+$	375
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{THF})]^-$	395, 330
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{PPh}_3)]^-$	450 sh, 395
$[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})_2]$	390
$[\text{Re}_2(\text{CO})_6(i\text{-Pr-PyCa})_2]$	785
$[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})]^-$	510, 285

The shift of these frequencies with respect to those of $[\text{Re}(\text{CO})_3(\text{N,N-dapa})(\text{P}(\text{OMe})_3)]$ (see Table 3) is almost equal to the frequency shifts observed upon the reduction of $[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]$ to give $[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]^-$ (see Table 2). The above frequencies are therefore assigned to the doubly reduced six-coordinated $[\text{Re}(\text{CO})_3(\text{N,N-dapa})(\text{P}(\text{OMe})_3)]^-$ complex. This means that one of the coordinated $\text{P}(\text{OMe})_3$ ligands is substituted by CO, still present in the thin solution layer of the OTTLE cell.

Two different anionic complexes were obtained by one-electron reduction of $[\text{Re}(\text{CO})_3(\text{N,N,N-dapa})]$. In $n\text{-PrCN}$ at 233–293 K, the six-coordinated anion $[\text{Re}(\text{CO})_3(\text{N,N-dapa})(n\text{-PrCN})]^-$ ($\nu(\text{CO})$ at 1980, 1856, and 1842 cm^{-1} , 233 K) was most likely formed as the only, stable product which did not even react with a 100-fold excess of PPh_3 . In THF at 293 K, another species was generated which exhibited $\nu(\text{CO})$ bands at 1964, 1856, and 1840 cm^{-1} , i.e. at much lower wavenumbers than those of six-coordinated $[\text{Re}(\text{CO})_3(\text{N,N-dapa})(n\text{-PrCN})]^-$, but at apparently higher wavenumbers than those of the five-coordinated, closely related anion $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})]^-$ (see Table 1). We therefore attribute the $\nu(\text{CO})$ frequencies in THF to a six-coordinated anion $[\text{Re}(\text{CO})_3(\text{N,N,N-dapa})]^-$, in which, however, coordination of the third N-atom of dapa to the Re center is very weak.

Scheme 6 summarizes the reduction pathways of $[\text{Re}(\text{CO})_3(\text{N,N-dapa})\text{L}']$ ($\text{L}' = \text{Br}^-$, Otf^-) in THF or $n\text{-PrCN}$ in the absence (A) and presence (B) of PPh_3 or $\text{P}(\text{OMe})_3$.

UV/Vis Spectroelectrochemistry. Several redox reactions described in the preceding section were also followed by UV/vis spectroscopy under the same conditions (concentration, temperature). The UV/vis data of the starting complexes and the products are summarized in Tables 4–6.

The $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{Br}]$ complexes under study show one ($\alpha\text{-diimine} = \text{bpy}$, $i\text{-Pr-PyCa}$, dapa) or two ($\alpha\text{-diimine} = \text{dpp}$, abpy) absorption bands in the visible region. The lowest energy bands of all parent complexes belong to CT transitions from π -interacting Re d_{π} -halide p_{π} orbitals to the lowest π^* orbital of $\alpha\text{-diimine}$ (L) (i.e. to transitions of a mixed MLCT/LCT character).²⁶ For $[\text{Re}(\text{CO})_3(\text{dpp})\text{Cl}]$, the band at higher energy

Table 5. Absorption Maxima in the Visible Region of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']$ ($\text{L}' = \text{Br}^-$, Otf^- ; $\alpha\text{-Diimine} = \text{dpp}$, abpy) and Their Reduction Products in THF

complex	λ_{max} (nm)
$[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]$	415, 320 sh
$[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]^-$	425, 310
$[\text{Re}(\text{CO})_3(\text{dpp})(\text{THF})]^-$	425, 310
$[\text{Re}(\text{CO})_3(\text{dpp})(\text{PPh}_3)]^-$	450
$[\text{Re}(\text{CO})_3(\text{dpp})]^-$	530, 410 sh, 320
$[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]$	570, 345
$[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^-$	500, 380
$[\text{Re}(\text{CO})_3(\text{abpy})(\text{THF})]^-$	470, 350 sh, 290
$[\text{Re}(\text{CO})_3(\text{abpy})\cdots\text{THF}]^{2-}$	480, 360

Table 6. Absorption Maxima in the Visible Region of $[\text{Re}(\text{CO})_3(\text{N,N-dapa})\text{L}']$ ($\text{L}' = \text{Br}^-$, Otf^-) and Their Reduction Products in THF

complex	λ_{max} (nm)
$[\text{Re}(\text{CO})_3(\text{N,N-dapa})\text{Br}]$	415
$[\text{Re}(\text{CO})_3(\text{N,N-dapa})(\text{Otf})]$	375
$[\text{Re}(\text{CO})_3(\text{N,N,N-dapa})]^+$	390
$[\text{Re}(\text{CO})_3(\text{N,N-dapa})(\text{PPh}_3)]^+$	375
$[\text{Re}(\text{CO})_3(\text{N,N,N-dapa})]^-$	405
$[\text{Re}(\text{CO})_3(\text{N,N-dapa})(\text{PPh}_3)]^-$	430
$[\text{Re}(\text{CO})_3(\text{N,N,N-dapa})]^{2-}$	540

has been assigned to an intraligand $\pi \rightarrow \pi^*$ transition of the dpp ligand.¹⁰

Upon the one-electron reduction of $[\text{Re}(\text{CO})_3(\text{bpy})\text{L}']$ ($\text{L}' = \text{Cl}^-$, Br^- , I^- , Otf^-) the metal-metal-bonded dimer $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$ was formed, which shows an intense band at 805 nm, and two weaker bands at 600 and 470 nm, respectively (Figure 4B). The 805 nm band most probably belongs to Re $d_{\pi} \rightarrow \pi^*$ (bpy) MLCT transitions,¹⁵ analogous to the related $[\text{Mn}_2(\text{CO})_6(\text{bpy})_2]$ dimer.²⁷ One-electron reduction of $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})\text{L}']$ ($\text{L}' = \text{Br}^-$, Otf^-) only produced a very small amount of $[\text{Re}_2(\text{CO})_6(i\text{-Pr-PyCa})_2]$ which showed again a low-energy band at 785 nm. For the C-C-coupled dimer $[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})_2]$, formed as the main product, the lowest-energy MLCT transition had shifted to 390 nm due to loss of conjugation between the pyridine and imine groups.

The final reduction product, the five-coordinated anion $[\text{Re}(\text{CO})_3(\text{bpy})]^-$, exhibits a broad and intense absorption band at 560 nm with shoulders at 630, 680, and 750 nm (Figure 4B). Similarly, $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})\text{L}']$ ($\text{L}' = \text{Br}^-$, Otf^-) and $[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]$ afforded the five-coordinated anions $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})]^-$ (λ_{max} 510 nm) and $[\text{Re}(\text{CO})_3(\text{dpp})]^-$ (λ_{max} 530, 410 (sh), 320 nm), respectively. The absorption band between 500 and 600 nm might be assigned either to an intraligand transition in the $\alpha\text{-diimine}$ ligand or, more probably, to an electronic transition with a partial $\text{bpy}^{2-} \rightarrow \text{Re}^{\text{I}}$ CT character.²²

The UV/vis spectra of the reduction products formed in the course of the successive reduction of $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]$ in THF, i.e. those of the radical anion $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^-$, the anion $[\text{Re}(\text{CO})_3(\text{abpy})(\text{THF})]^-$, and the dianion $\{[\text{Re}(\text{CO})_3(\text{abpy})] \cdots \text{THF}\}^{2-}$, are depicted in Figure 3B.

Cyclic Voltammetry. Cyclic voltammograms of the complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}]^{0/+}$ ($\text{L}' = \text{Cl}^-$, Br^- , I^- , Otf^- , PPh_3) were recorded in THF. The electrode

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Table 7. Reduction Potentials (V vs Fc/Fc⁺) of the Complexes [Re(CO)₃(α-diimine)L]^{0/+j}

complex	<i>E</i> _{p,c} ^{I a}	(Δ <i>E</i> _p)	<i>E</i> _{p,c} ^{II a}
[Re(CO) ₃ (bpy)Cl]	-1.91	(110)	-2.38
[Re(CO) ₃ (bpy)Br]	-1.91	(110)	-2.33
[Re(CO) ₃ (bpy)I]	-1.91	(105)	-2.27
[Re ₂ (CO) ₆ (bpy) ₂] ^b	-2.08	(100)	
[Re(CO) ₃ (bpy)(Otf)] ^c	-1.54	(95)	
[Re(CO) ₃ (bpy)(THF)] ^{+ d}	-1.73	(75)	-2.23
[Re(CO) ₃ (bpy)(PPh ₃)] ^{+ e}	-1.62	(75)	-2.10
[Re(CO) ₃ (<i>i</i> -Pr-PyCa)Br]	-1.75	(90)	-2.37
[Re ₂ (CO) ₆ (C-C- <i>i</i> -Pr-PyCa) ₂]	-1.96		
[Re(CO) ₃ (<i>i</i> -Pr-PyCa)(Otf)] ^c	-1.36	(90)	
[Re(CO) ₃ (<i>i</i> -Pr-PyCa)(THF)] ^{+ d}	-1.64	(120)	-2.21
[Re(CO) ₃ (<i>i</i> -Pr-PyCa)(PPh ₃)] ^{+ e}	-1.45	(85)	-2.08
[Re(CO) ₃ (<i>N,N</i> -dapa)Br]	-1.64	(90)	-2.16
[Re(CO) ₃ (<i>N,N</i> -dapa)(Otf)] ^c	-1.29	(100)	
[Re(CO) ₃ (<i>N,N</i> -dapa)] ⁺	-1.59	(105)	-2.16
[Re(CO) ₃ (<i>N,N</i> -dapa)(POMe ₃)] ^{+ f}	-1.40	(70)	-1.95
[Re(CO) ₃ (<i>N,N</i> -dapa)(PPh ₃)] ^{+ e}	-1.35	(80)	-1.82
[Re(CO) ₃ (dpp)Br] ^g	-1.56	(80)	-2.05
[Re(CO) ₃ (abpy)Br] ^h	-0.80	(90)	-1.49
[Re(CO) ₃ (abpy)(Otf)] ^c	-0.46	(115)	
[Re(CO) ₃ (abpy)(THF)] ^{+ d,h}	-0.62	(70)	-1.36 ⁱ
[Re(CO) ₃ (abpy)(PPh ₃)] ^{+ e,h}	-0.51	(80)	-1.46 ⁱ

^a Peak potentials of the first and second reductions. ^b Oxidation of [Re₂(CO)₆(bpy)₂] at -0.29 and -0.60 V vs Fc/Fc⁺. ^c No second reduction observed. ^d Measured in situ in a [Re(CO)₃(α-diimine)(Otf)]/THF solution. ^e Measured in situ in a [Re(CO)₃(α-diimine)(Otf)]/excess PPh₃/THF solution. ^f Measured in situ in a [Re(CO)₃(abpy)(Otf)]/excess POMe₃/THF solution. ^g Both in the absence and presence of excess PPh₃. ^h A third, electrochemically quasireversible, chemically reversible reduction at *E*_{p,c} = -2.86 V vs Fc/Fc⁺. ⁱ Δ*E*_p = 90 mV. ^j CV of 10⁻³ M solutions in THF/10⁻¹ M Bu₄NPF₆ at *v* = 100 mV/s, 0.8 mm² Pt disk electrode, 293 K.

potentials, presented in Table 7, were measured against the standard Fc/Fc⁺ redox couple.^{13,28}

The cyclic voltammograms (CV) of the complexes [Re(CO)₃(α-diimine)Br] (α-diimine = bpy, *i*-Pr-PyCa, dapa, dpp), measured without excess Br⁻ in the THF solution, exhibited two one-electron cathodic peaks separated by approximately 400–600 mV (see Table 7). The only exception was the CV of the complex [Re(CO)₃(abpy)Br] in which the two cathodic peaks were found at significantly more positive potentials (Table 7) and were separated by 690 mV (see Figure 5A). In this case, even a third cathodic peak appeared at *E*_{p,c} = -2.86 V.

On the basis of previous results,^{2d,f,k,3b,d} the first reduction is assigned to

For all [Re(CO)₃(α-diimine)Br] studied, this process was electrochemically reversible and diffusion controlled, as evidenced by identical or slightly different Δ*E*_p values for the [Re(CO)₃(α-diimine)Br]/[Re(CO)₃(α-diimine)Br]^{•-} and Fc/Fc⁺ redox couples²⁸ and by a constant value of the current function *i*_p*v*^{-1/2}, respectively. The reduction was chemically reversible on the CV time scale, corresponding to the scan rate range of *v* = 50–500 mV/s, only for the complexes [Re(CO)₃(α-diimine)Br], α-diimine = dpp and abpy (the current ratio *i*_p^a/*i*_p^c = 1). The one-electron reduction of these two [Re(CO)₃(α-diimine)Br] complexes was chemically reversible even in the presence of a 100-fold excess of PPh₃ in the THF

(28) Electrochemical reversibility of all electrode processes was compared with that of the Fc/Fc⁺ couple in the same solution to account for effects such as uncompensated iR drop, electrode passivation, etc.

Figure 5. Cyclic voltammogram of [Re(CO)₃(abpy)Br] in the absence (A) and presence (B) of PPh₃. Conditions: 10⁻³ M solution in THF/10⁻¹ M Bu₄NPF₆ (A), and 10⁻¹ M PPh₃ (B); Pt disk electrode, 293 K, *v* = 100 mV/s.

solution. This observation is in full agreement with the IR spectroelectrochemical results (see above) which indicated only slow substitution of Br⁻ by THF (α-diimine = dpp) or by PPh₃ (α-diimine = dpp, abpy).

The radical anions [Re(CO)₃(α-diimine)Br]^{•-} (α-diimine = bpy, *i*-Pr-PyCa, dapa) were not stable on the CV time scale (*i*_p^a/*i*_p^c was less than 1 within *v* = 50–500 mV/s and did not change significantly with the increasing scan rate). On the reverse scan, a small anodic peak appeared in all cyclic voltammograms at a more positive potential than that of the anodic counterpeak of the [Re(CO)₃(α-diimine)Br]/[Re(CO)₃(α-diimine)Br]^{•-} redox couple. On the basis of the IR OTTLE results (see above) and on comparison with cyclic voltammograms of the related complexes [Re(CO)₃(α-diimine)(Otf)] (see below, Table 7), the small anodic peaks are assigned to reoxidation of the radicals [Re(CO)₃(α-diimine)(THF)][•] (α-diimine = bpy, *i*-Pr-PyCa) and [Re(CO)₃(*N,N,N*-dapa)][•], formed from the labile radical anions [Re(CO)₃(α-diimine)Br]^{•-} by dissociation of Br⁻ and rapid coordination of the solvent or the third nitrogen atom of the dapa ligand, respectively. It is noteworthy that the radical [Re(CO)₃(bpy)(THF)][•] was not detected on the OTTLE time scale due to its fast conversion to [Re₂(CO)₆(bpy)₂] (see above). The formation of the dimer on the CV time scale was revealed by the presence of two additional anodic peaks in the CV of [Re(CO)₃(bpy)Br] at *E*_{p,a} = -0.60 and -0.29 V,

observed on the reverse scan after passing the first cathodic process, and a new, electrochemically reversible, redox couple at $E_{1/2} = -2.03$ V, observed during repeated potential sweeps between the two cathodic processes of parent $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{Br}]$ (Table 7). In accordance with literature data, the chemically irreversible anodic processes^{2f} are assigned to

and

respectively. Both positively charged dimers readily decompose to give parent $[\text{Re}(\text{CO})_3(\text{bpy})\text{Br}]$, the only product detected on the IR OTTLE time scale. The redox couple at -2.03 V is attributed^{2d,f,k} to

No peaks due to redox reactions of $[\text{Re}(\text{CO})_3(\text{bpy})\text{-(THF)}]^-$ and $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$ were found in the CV of $[\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}]$. The one-electron reduction of this complex (Table 7) was chemically reversible on the CV time scale ($i_p^a/i_p^c = 1$) having thus manifested, in accordance with the IR OTTLE experiments, higher stability of $[\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}]^-$ in comparison with the Br derivative.

In the presence of PPh_3 , one-electron reduction of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{Br}]$ ($\alpha\text{-diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{dapa}$) led to the stable radicals $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{PPh}_3)]$ (see the IR OTTLE results). In the corresponding cyclic voltammograms, the fast follow-up conversion of the primary reduction product $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{Br}]^-$ to $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{PPh}_3)]$ was again evidenced by the appearance of small anodic peaks after switching the scan direction behind the cathodic peak of the chemically irreversible reduction of parent $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{Br}]$. These small peaks could reasonably be assigned to reoxidation of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{PPh}_3)]$ as their $E_{p,a}$ values agreed well with those obtained from cyclic voltammograms of corresponding $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{PPh}_3)]^+$ (see below, Table 7). For $\alpha\text{-diimine} = \text{bpy}$, all CV peaks of $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$ (Table 7) disappeared upon addition of PPh_3 , in line with the spectroelectrochemical results described in preceding sections.

The second, more negative, redox couple in the CV of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{Br}]$ ($\alpha\text{-diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{dapa}, \text{dpp}, \text{abpy}$) (Table 7) was chemically irreversible ($i_p^a/i_p^c < 1$), independent of $\alpha\text{-diimine}$ or addition of excess PPh_3 into the THF solution (see Figure 5A). The irreversibility may best be explained by attributing^{2d,f,k} the second reduction step to

As evidenced by the spectroelectrochemical results, the doubly reduced complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{Br}]^{2-}$ are extremely labile and readily lose Br^- to give either five-coordinated anions $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})]^-$ ($\alpha\text{-diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{dpp}$) or six-coordinated anions

Figure 6. Cyclic voltammogram of $[\text{Re}(\text{CO})_3(\text{bpy})(\text{Otf})]$. Conditions: 10^{-3} M solution in THF/ 10^{-1} M Bu_4NPF_6 , Pt disk electrode, 293 K, $\nu = 100$ mV/s; * = Fc/Fc^+ .

$[\text{Re}(\text{CO})_3(\text{abpy})\text{L}']$ ($\text{L}' = \text{THF}, \text{PPh}_3$). The remaining anion in the series, $[\text{Re}(\text{CO})_3(\text{N,N}(\text{N})\text{-dapa})]^-$, can be considered as a transient case (see above). All anions should undergo one-electron reoxidation which, however, was not clearly detectable in the cyclic voltammograms of most $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{Br}]$ studied. An exception is the cyclic voltammogram of $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]$ (Figure 5A) which exhibits a small, positively shifted, anodic peak at -1.22 V which can reasonably be assigned to the reoxidation of stable $[\text{Re}(\text{CO})_3(\text{abpy})\text{-(THF)}]^-$. For, the chemically reversible redox couple $[\text{Re}(\text{CO})_3(\text{abpy})(\text{THF})]/[\text{Re}(\text{CO})_3(\text{abpy})(\text{THF})]^-$ was found at $E_{1/2} = -1.31$ V ($\Delta E_p = 90$ mV) in the cyclic voltammogram of $[\text{Re}(\text{CO})_3(\text{abpy})(\text{Otf})]$ in THF (see below). The small difference in $E_{p,a}$ can be ascribed to an influence of kinetics of the irreversible reduction of $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^-$, involving dissociation of Br^- from $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^{2-}$ and concomitant coordination of THF.

The one-electron reduction of $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^-$ in the presence of excess PPh_3 appeared to be chemically reversible ($i_p^a/i_p^c = 1$ within $\nu = 20\text{--}500$ mV/s) (see B in Figure 5B), which seemed to be in contradiction with the above interpretation. However, the reversible redox couple B in Figure 5B is in fact composed of two different redox couples, $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^-/[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^{2-}$ and $[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]/[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]^-$, that accidentally coincide (see Table 7).

Both six-coordinated anions $[\text{Re}(\text{CO})_3(\text{abpy})\text{L}']^-$ ($\text{L}' = \text{THF}, \text{PPh}_3$) could subsequently be reduced at -2.86 V in an electrochemically quasireversible ($\Delta E_p = 130$ mV vs 90 mV for Fc/Fc^+ and chemically reversible ($i_p^a/i_p^c = 1$ at $\nu = 100$ mV/s) one-electron step to give, according to the IR OTTLE results (see above), the stable dianions $\{[\text{Re}(\text{CO})_3(\text{abpy})]^{2-} \cdots \text{L}'\}$. Very weak coordination of L' to the Re center in the dianions, as evidenced by their very similar average CO force constants (see Table 2), is probably responsible for the observed electrochemically quasireversible character of this reduction step.

Cyclic voltammograms of the complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{Otf})]$ ($\alpha\text{-diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{dapa}$ and abpy) in THF are, in general, more complex than those of corresponding $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{Br}]$. They exhibit three characteristic cathodic peaks (denoted as A, B, and D, see Figure 6) which were accompanied, in the case of $\alpha\text{-diimine} = \text{bpy}$ and $i\text{-Pr-PyCa}$, by a fourth cathodic peak at -2.08 (C in Figure 6) and -1.96 V, respectively.

The cathodic peak current, $i_{p,c}$, of the redox couples B and D was typically observed to be significantly lower in comparison with $i_{p,c}$ of the most positive redox couple A (see Figure 6). This means that the cathodic peak of the redox couple A can be assigned to one-electron reduction of parent $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{Otf})]$ (see Table 7). The reduction is followed by a secondary reaction producing a species which can successively be reduced at more negative potentials.

The IR OTTLE experiments have demonstrated that $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{Otf})]$ ($\alpha\text{-diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{abpy}$) are converted in an electrochemically initiated electron-transfer chain (ETC) step to the corresponding cations $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{THF})]^+$. In these cases, we therefore attribute the redox couples B and D to

and

respectively (see Table 7). A similar reaction sequence can be applied for $[\text{Re}(\text{CO})_3(N,N\text{-dapa})(\text{Otf})]$ which is reduced at -1.29 V. On the basis of the IR OTTLE experiments (see above), the reduction initiated transformation of $[\text{Re}(\text{CO})_3(N,N\text{-dapa})(\text{Otf})]$ to $[\text{Re}(\text{CO})_3(N,N,N\text{-dapa})]^+$ which was subsequently reduced in two steps to give $[\text{Re}(\text{CO})_3(N,N,N\text{-dapa})]^\bullet$ and $[\text{Re}(\text{CO})_3(N,N,N\text{-dapa})]^-$. These reductions were observed in the CV of $[\text{Re}(\text{CO})_3(N,N\text{-dapa})(\text{Otf})]$ as two cathodic peaks at -1.59 V (B) and -2.16 V (D), respectively.

Comparison of the cyclic voltammograms of $[\text{Re}(\text{CO})_3(\text{bpy})\text{L}']$ ($\text{L}' = \text{Br}^-$ and Otf^-) revealed, in accordance with literature data,^{2d,f,k} that the redox couple C in the CV of $[\text{Re}(\text{CO})_3(\text{bpy})(\text{Otf})]$ (see Figure 6) can be assigned according to eq 5. In agreement with this assignment, the two successive oxidations of $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$, as described by eqs 3 and 4, were also found in the CV of $[\text{Re}(\text{CO})_3(\text{bpy})(\text{Otf})]$ at -0.51 and -0.23 V, respectively (Figure 6). Similarly, the cathodic peak of the redox couple C in the CV of related $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})(\text{Otf})]$ was assigned to one-electron reduction of the C-C-coupled dimer $[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})_2]$ (Table 7), the major product formed upon the reduction of the parent complex (see above). It is important to note that the cathodic peak C of $[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})_2]$ was much less developed than that of $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$ under identical conditions, i.e. concentration of parent $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{Otf})]$, temperature, scan rate. This observation is not surprising, as it is likely to assume that the formation of $[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})_2]$ is a slower process than the formation of the metal-metal-bonded dimer $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$.

In the presence of excess PPh_3 , all complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{Otf})]$ ($\alpha = \text{bpy}, i\text{-Pr-PyCa}, \text{dapa}, \text{abpy}$) were thermally converted to $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{PPh}_3)]^+$ prior to the CV experiments. Consequently, only two redox couples were observed during negative CV scans (see Table 7) which are assigned to

and

The second reduction (10) was chemically and electrochemically reversible only for $\alpha\text{-diimine} = \text{abpy}$. This result once more confirms the inherent stability of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{PPh}_3)]^-$, as was revealed by the above described IR OTTLE experiments.

Discussion

The experimental results clearly show that the nature of the products, formed by reduction of the complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']^{0/+}$, is mainly determined by the $\alpha\text{-diimine}$ ligand. A schematic MO diagram of the parent complexes is presented in Figure 7.

The relative positions of the orbitals are derived from MO calculations performed on $[\text{Mn}(\text{CO})_3(\text{bpy})\text{L}']$ complexes ($\text{L}' = \text{Cl}^-, \text{Br}^-, \text{I}^-$).²⁶ The HOMO consists of two close-lying orbitals which are an antibonding $\text{Re } d_{\pi}\text{-L}' p_{\pi}$ combination with a variable halide p_{π} contribution. Apart from this weak π interaction, there is a much stronger $\text{Re-L}' \sigma$ interaction, giving rise to a filled bonding orbital and an empty antibonding orbital, which are mainly $\text{L}' p\sigma$ and $\text{Re } d\sigma^*$ in character, respectively. The LUMO is mainly $\alpha\text{-diimine } \pi^*$ in character. The energy of the π^* LUMO decreases in the order $\text{bpy} > i\text{-Pr-PyCa} > \text{dapa} > \text{dpp} > \text{abpy}$, as evidenced by both the shift of the CT band of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']^{0/+}$ to higher energy (Tables 4–6) and the negative shift of the one-electron reduction potential of these complexes (Table 7) in the same order. The lower the energy of the π^* orbital, the better the $\alpha\text{-diimine}$ ligand is able to accommodate the added electron(s). The stability of the products of the first, second, and (for abpy) third one-electron reduction steps is strongly influenced by this property and will be discussed in this section.

The First One-Electron Reduction Step. One-electron reduction of the complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']^{0/+}$ destabilizes the π^* LUMO of the $\alpha\text{-diimine}$ ligand, which is expected to accommodate the unpaired electron. However, the resulting decrease of the $\nu(\text{CO})$ frequencies by $20\text{--}30 \text{ cm}^{-1}$ clearly points to an increase of the electron density also on Re and the CO ligands. In full line with the Koopmans theorem, the relative energies of the frontier orbitals are not considerably changed upon reduction and the electronic effects are delocalized over the whole complex. Only the π^* SOMO of the $\alpha\text{-diimine}$ ligand is slightly shifted to higher energy, for example in comparison with the empty $d\sigma^*$ orbital. Hence, the observed labilization of the $\text{Re-L}'$ bond is ascribed to profound changes in the $\alpha\text{-diimine}$ nature, from a π acceptor in $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']^{0/+}$ to a rather strong σ donor in the $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']^{-/+}$ products. Its extent appears to increase with a negative shift in the one-electron reduction potential of the parent complexes which reflects a lower tendency of $\alpha\text{-diimine}$ to accommodate the unpaired electron. The most labile $\text{Re-L}'$ bonds can therefore be expected for

Figure 7. Schematic MO diagram of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L'}]^{0/+}$, derived from MO calculations performed²⁶ on $[\text{Mn}(\text{CO})_3(\text{bpy})\text{L}']$ ($\text{L}' = \text{Cl}^-, \text{Br}^-, \text{I}^-$).

the reduction products with the bpy and *i*-Pr-PyCa ligands, especially if L' is a negatively charged halide or a hard Lewis base like THF.

Indeed, one-electron reduction of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L'}]^{0/+}$ ($\text{L}' = \text{halide, THF; } \alpha\text{-diimine} = \text{bpy, } i\text{-Pr-PyCa}$) resulted in the fast dissociation of L' from $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L'}]^{-\bullet}$. For $\alpha\text{-diimine} = \text{bpy}$, the $[\text{Re}(\text{CO})_3(\text{bpy})]^{-\bullet}$ radicals readily dimerized to give the metal-metal-bonded complex $[\text{Re}_2(\text{CO})_6(\text{bpy})_2]^-$, whereas the $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})]^{-\bullet}$ radicals reacted to give the C-C-coupled dimer $[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})_2]$ as the main product, together with a very small amount of the metal-metal-bonded dimer $[\text{Re}_2(\text{CO})_6(i\text{-Pr-PyCa})_2]$. Obviously, the *i*-Pr-PyCa ligand in $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})]^{-\bullet}$ tends to accommodate the unpaired electron in the π^* orbital localized mainly on the nonaromatic imine group which exerts higher reactivity toward a C-C-coupling reaction than an aromatic imine group.

The observed slow substitution of Br^- by THF in the $[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]^{-\bullet}$ radical anion indicates that the Re-Br bond is still considerably labilized. The reduction potential of $[\text{Re}(\text{CO})_3(\text{dpp})(\text{THF})]^+$ is expected to be more positive than that of $[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]$, as observed for the analogous bpy and *i*-Pr-PyCa complexes (Table 7). Apparently, the dpp radical ligand is still a sufficiently strong donor in the $[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]^{-\bullet}$ radical anion to cause dissociation of the negatively charged Br^- ligand. This reasonably explains the observed lability of $[\text{Re}(\text{CO})_3(\text{dpp})\text{Br}]^{-\bullet}$ toward the attack of THF. The donor power of the dpp radical anion in the product $[\text{Re}(\text{CO})_3(\text{dpp})\text{THF}]$ decreases to such an extent that the Re-THF bond is relatively stable.

One-electron reduction of $[\text{Re}(\text{CO})_3(\text{abpy})\text{L'}]^{0/+}$ ($\text{L}' = \text{Br}^-, \text{THF}$) gave rise to the formation of the stable $[\text{Re}(\text{CO})_3(\text{abpy})\text{L'}]^{-\bullet}$ complexes. In this case, the rather positive reduction potentials of the parent species indicate that the added electron is completely localized on the azo bond of the abpy ligand. The polarization effect of the abpy radical on the Re-Br bond in $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^{-\bullet}$ is therefore very limited and the complex is able to withstand the attack of THF.

The same arguments can be used to explain the experimentally observed stability of the radicals $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{PPh}_3)]^{-\bullet}$ ($\alpha\text{-diimine} = \text{bpy, } i\text{-Pr-PyCa, dpp, and abpy}$). The π^* LUMO of the $\alpha\text{-diimine}$ is relatively low in energy in the parent complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{PPh}_3]^+$ (see Table 7), thereby making it more able to accommodate the unpaired electron. Also, the Re-PPh₃ bond is more resistant toward a cleavage in comparison with the THF and Br^- ligands due to the stronger π acceptor and weaker σ donor character of PPh₃. Consequently, it is not surprising that, although $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^{-\bullet}$ is stable enough to withstand the substitution of Br^- by THF (vide supra), the Re-Br bond is labilized sufficiently for the substitution of Br^- by PPh₃. This experimental result is fully in accord with the above interpretation. In this respect, an even higher stability can be predicted for the axial Re-CO bond in the $[\text{Re}(\text{CO})_4(\alpha\text{-diimine})]^{-\bullet}$ radicals. Recent electrochemical results on $[\text{Re}(\text{CO})_4(\text{bpy})]^+$ seem to support this trend.²⁹

The increased localization of the unpaired electron on the $\alpha\text{-diimine}$ should also be reflected in an increase of the CO-stretching frequencies and k_{av} for the $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{Br}]^{-\bullet}$ and $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{PPh}_3)]^{-\bullet}$ radicals in the order $\alpha\text{-diimine} = \text{bpy} < i\text{-Pr-PyCa} < \text{dpp} < \text{abpy}$. With the exception of the complexes with the bpy ligand, all reduced complexes indeed comply with this expected trend (Tables 1–3).

The Second One-Electron Reduction Step. One-electron reduction of the metal-metal-bonded dimer $[\text{Re}_2(\text{CO})_6(\alpha\text{-diimine})_2]$ ($\alpha\text{-diimine} = \text{bpy, } i\text{-Pr-PyCa}$) resulted in the formation of the five-coordinated anionic $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})]^-$ complex. This reduction step is localized with all probability on the $\alpha\text{-diimine } \pi^*$ LUMO of the dimers. As a consequence of the strong polarization effect caused by a considerable σ -donor character of coordinated bpy^- and *i*-Pr-PyCa⁻ (see above), the Re-Re bond in $[\text{Re}_2(\text{CO})_6(\alpha\text{-diimine})_2]^-$ is rapidly split upon generation of both the five-coordinated anionic $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})]^-$ and radical $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})]^{-\bullet}$ complexes. The latter radical complex is readily reduced at the applied potential to give $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})]^-$. Alternatively, the radical dimeric species $[\text{Re}_2(\text{CO})_6(\alpha\text{-diimine})_2]^{-\bullet}$ might be stable, so that a second one-electron reduction is needed to induce the splitting of the Re-Re bond. However, the experimental results are not in favor of the latter explanation, since reduced $[\text{Re}_2(\text{CO})_6(\alpha\text{-diimine})_2]^{-\bullet}$ were not detected in the course of the spectroelectrochemical experiments, but only on the CV time scale. Similarly, it has recently been shown that the related metal-metal-bonded complexes $[(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})]$ were readily split into $[\text{Mn}(\text{CO})_5]^-$ and $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})]^{-\bullet}$ upon one-electron reduction.³⁰

One-electron reduction of the C-C-coupled $[\text{Re}_2(\text{CO})_6(\text{C-C-}i\text{-Pr-PyCa})_2]$ dimer was also shown to produce the five-coordinated $[\text{Re}(\text{CO})_3(i\text{-Pr-PyCa})]^-$ complex. The mechanism of this reaction remains to be established.

One-electron reduction of $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L'}]^{-\bullet}$ ($\text{L}' = \text{PPh}_3, \alpha\text{-diimine} = \text{bpy, } i\text{-Pr-PyCa, dpp; } \text{L}' = \text{THF, } \alpha\text{-diimine} = \text{dpp}$) also led to the formation of the five-coordinated anionic $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})]^-$ complex. Apparently, the donor ability of the $\alpha\text{-diimine}$ dianionic ligand in $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})]^-$ is extremely enhanced. It prevents even the coordination of PPh₃ as a weak π -acceptor molecule, which occurs during the first one-electron reduction step. Instead, a strong π -interaction

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may take place between the π^* HOMO of the α -diimine dianion and the asymmetric member of the set of LUMO orbitals of the $\text{Re}(\text{CO})_3^+$ fragment, like in the isoelectronic $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ ²² and $[\text{W}(\text{CO})_3(\text{DBCat})]^{2-}$ ²³ (DBCat = 3,5-di-*tert*-butylcatecholate) complexes. This interaction in the five-coordinated $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})]^-$ anion allows the α -diimine dianion to exert very strong π -donor character and to increase considerably the electron density on Re. Experimentally, this π -delocalization is evidenced by much lower $\nu(\text{CO})$ frequencies and average CO force constants of the $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})]^-$ anions in comparison with the stable six-coordinated anions $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']^-$ (α -diimine = dapa, $\text{L}' = \text{P}(\text{OMe})_3$, *n*-PrCN; α -diimine = abpy, $\text{L}' = \text{THF}$, PPh_3) (Tables 1–3).

One-electron reduction of $[\text{Re}(\text{CO})_3(\text{abpy})\text{Br}]^-$ or $[\text{Re}(\text{CO})_3(\text{abpy})(\text{THF})]^-$ produced the doubly reduced six-coordinated $[\text{Re}(\text{CO})_3(\text{abpy})(\text{THF})]^{2-}$ complex. The six-coordinated geometry of the latter anionic complex indicates a relatively low donor ability of the abpy dianion. This implies that both added electrons are accommodated completely in the lowest π^* orbital of the abpy ligand localized³¹ on its azo bond. Such a distribution of the electron density over the abpy ligand induces only the dissociation of the negatively charged halide, but the Re–THF bond remains thermally stable. The one-electron reduction of $[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]^-$ to give $[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]^{2-}$ may obviously be explained in the same way.

The Third One-Electron Reduction Step. The third reduction step at rather negative potentials was observed only for the abpy complexes. One-electron reduction of $[\text{Re}(\text{CO})_3(\text{abpy})(\text{THF})]^-$ or $[\text{Re}(\text{CO})_3(\text{abpy})(\text{PPh}_3)]^-$ resulted in the formation of complexes with slightly different CO-stretching frequencies. Therefore, it was decided that $\{[\text{Re}(\text{CO})_3(\text{abpy})]^{2-} \cdots \text{THF}\}$ and $\{[\text{Re}(\text{CO})_3(\text{abpy})]^{2-} \cdots \text{PPh}_3\}$ were formed, respectively. The weak interaction of the donor solvent and/or phosphine molecule with five-coordinated $[\text{Re}(\text{CO})_3(\text{abpy})]^{2-}$ suggests that the abpy ligand can partly accommodate even the third added electron, probably on the pyridyl rings. Thus, only the third reduction step led in this case to the splitting of the Re– L' bond ($\text{L}' = \text{THF}$, PPh_3). This behavior reflects the considerably increased π -donor character of formally abpy^{3-} , which corresponds to the population of another π^* orbital of much higher energy. Noteworthy, two one-electron and one two-electron reduction steps, localized on abpy, have recently been reported³¹ for the $[(\text{Ru}(\text{bpy})_2)_2(\mu\text{-abpy})]^{4+}$ complex. The exceptional π -acceptor ability of the bridging, easily reducible abpy ligand has been explained by a considerably low energy of its frontier π^* orbitals.

The $[\text{Re}(\text{CO})_3(\text{N,N-dapa})\text{L}']$ ($\text{L}' = \text{Br}^-$, Otf^-) Complexes. The energy of the π^* SOMO of the dapa ligand in the complexes $[\text{Re}(\text{CO})_3(\text{N,N-dapa})\text{L}']^{0/+}$ is comparable with the energy of the π^* SOMO of *i*-Pr-PyCa (Table 7). Nevertheless, no dimeric products, characteristic for the *i*-Pr-PyCa complexes, were formed upon one-electron reduction of $[\text{Re}(\text{CO})_3(\text{N,N-dapa})\text{Br}]$. Apart from possible, but less important steric reasons, this is presumably due to the ability of the third nitrogen atom of the dapa ligand to coordinate at the open site on the Re center, created by dissociation of Br^- from $[\text{Re}(\text{CO})_3$ -

$(\text{N,N-dapa})\text{Br}]^-$. This was manifested by the one-electron reduction of $[\text{Re}(\text{CO})_3(\text{N,N-dapa})\text{L}']^{0/+}$ ($\text{L}' = \text{Br}^-$, Otf^-) in the presence of excess PPh_3 . Although in both reactions the $[\text{Re}(\text{CO})_3(\text{N,N-dapa})(\text{PPh}_3)]^-$ complex was formed as the main product, the $[\text{Re}(\text{CO})_3(\text{N,N-dapa})]^-$ complex was observed as the second, minor product. It is obvious from these results that the third nitrogen atom of the reduced dapa ligand can compete even with PPh_3 for coordination at the open site on Re, due to energetically convenient closure of the second chelate bond.

In view of the above-mentioned, it is not surprising that the one-electron reduction of the radical complexes $[\text{Re}(\text{CO})_3(\text{N,N,N-dapa})]^-$ and $[\text{Re}(\text{CO})_3(\text{N,N-dapa})(\text{PPh}_3)]^-$ gave rise to the formation of the anionic $[\text{Re}(\text{CO})_3(\text{N,N,N-dapa})]^{2-}$ complex. Due to the same reasons as already discussed for the analogous $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})(\text{PPh}_3)]^-$ (α -diimine = bpy, *i*-Pr-PyCa, dpp) complexes, $[\text{Re}(\text{CO})_3(\text{N,N-dapa})(\text{PPh}_3)]^-$ loses the PPh_3 ligand after one-electron reduction. Like the *i*-Pr-PyCa dianion, coordinated dapa^{2-} also possesses strong donor character, which in turn makes the interaction of its third nitrogen with the Re center in $[\text{Re}(\text{CO})_3(\text{N,N,N-dapa})]^{2-}$ rather weak.

One-electron reduction of $[\text{Re}(\text{CO})_3(\text{N,N-dapa})(\text{P}(\text{OMe})_3)]^+$ in the presence of excess $\text{P}(\text{OMe})_3$ produced $[\text{Re}(\text{CO})_3(\text{N,N-dapa})(\text{P}(\text{OMe})_3)]^-$. Subsequently, this complex readily transformed into $[\text{Re}(\text{CO})_2(\text{N,N-dapa})(\text{P}(\text{OMe})_3)_2]^-$. Recently, a similar reduction-induced CO-substitution reaction has been observed³² for $[\text{Ru}(\text{CO})_2(\text{i-Pr-DAB})(\text{Me})(\text{P}(\text{OMe})_3)]^+$, which was reduced in the presence of excess $\text{P}(\text{OMe})_3$ to give $[\text{Ru}(\text{CO})_2(\text{i-Pr-DAB})(\text{Me})(\text{P}(\text{OMe})_3)_2]^-$. For both the Re and Ru complex, no CO substitution was observed in the presence of excess PPh_3 . This may be due to the stronger π -acceptor character and smaller cone angle of $\text{P}(\text{OMe})_3$ compared with PPh_3 . Nevertheless, the electron density on the Re center strongly increases upon substitution of CO by $\text{P}(\text{OMe})_3$, as displayed by the much lower k_{av} value of $[\text{Re}(\text{CO})_2(\text{N,N-dapa})(\text{P}(\text{OMe})_3)_2]^-$ ($k_{\text{av}} = 1460 \text{ Nm}^{-1}$) compared with $[\text{Re}(\text{CO})_3(\text{N,N-dapa})(\text{P}(\text{OMe})_3)]^-$ ($k_{\text{av}} = 1535 \text{ Nm}^{-1}$). Therefore, it is understandable that one-electron reduction of $[\text{Re}(\text{CO})_2(\text{N,N-dapa})(\text{P}(\text{OMe})_3)_2]^-$ leads to a dissociation of one of the $\text{P}(\text{OMe})_3$ ligands. Noteworthy, one $\text{P}(\text{OMe})_3$ ligand still remains coordinated in the anionic $[\text{Re}(\text{CO})_3(\text{N,N-dapa})(\text{P}(\text{OMe})_3)]^-$ product due to its significant π -acceptor character, which can compensate for the strongly increased donor power of dapa upon its reduction to formal dianion. The open site on the Re center is reoccupied by CO still present in the solution. A similar reaction has been observed for the $[\text{Re}(\text{CO})_2(\text{DBSQ})(\text{PPh}_3)_2]$ complex, which reacted to give $[\text{Re}(\text{CO})_3(\text{DBCat})(\text{PPh}_3)]^-$ upon one-electron reduction in the presence of CO.²¹ The reverse substitution of $\text{P}(\text{OMe})_3$ by CO strongly decreases the electron density in the Re d_π orbitals. This is evidenced by the increase of k_{av} when $[\text{Re}(\text{CO})_2(\text{N,N-dapa})(\text{P}(\text{OMe})_3)_2]^-$ ($k_{\text{av}} = 1460 \text{ Nm}^{-1}$) transforms into $[\text{Re}(\text{CO})_3(\text{N,N-dapa})(\text{P}(\text{OMe})_3)]^-$ ($k_{\text{av}} = 1490 \text{ Nm}^{-1}$), despite a second electron is added to the complex.

Summary and Conclusions

(1) The combination of cyclic voltammetry and in situ spectroelectrochemical FTIR and UV/vis measurements

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provided an excellent tool for the elucidation of the reduction pathways for a series of complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']^{0/+}$ ($\alpha\text{-diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{dapa}, \text{dpp}, \text{abpy}$; $\text{L}' = \text{Br}^-$, donor solvent, PR_3 , $\text{P}(\text{OR})_3$).

(2) The stability of the $\text{Re-L}'$ bond in the radical products of the first one-electron reduction, $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']^{-\cdot/}$, appeared to increase in the order $\text{bpy} < i\text{-Pr-PyCa} < \text{dapa} < \text{dpp} < \text{abpy}$, i.e. with the ability of the $\alpha\text{-diimine}$ ligand to accommodate the unpaired electron in its π^* LUMO, as was manifested by the less negative reduction potentials of the parent complexes and by the increasing CO force constants of the radical products in the same order.

(3) The second one-electron reduction step drastically destabilizes the coordination of the ligand L' and leads to the delocalized $\text{Re}-(\alpha\text{-diimine}^{2-}) \pi$ bonding in the five-coordinated anions $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})]^-$ ($\alpha\text{-diimine} = \text{bpy}, i\text{-Pr-PyCa}, \text{dpp}$).

(4) The six-coordinated anionic complexes $[\text{Re}(\text{CO})_3(\alpha\text{-diimine})\text{L}']^-$ may be formed under the following circumstances: (a) $\alpha\text{-diimine}$ accommodates completely both added electrons (abpy with the easily reducible azo bond); (b) L' is an efficient π -acceptor ligand like $\text{P}(\text{OR})_3$ or CO^{29} ; (c) L' is present in a very large excess (the $n\text{-PrCN}$ solvent); (d) $\alpha\text{-diimine}$ coordinates as a tripodate ligand (dapa: L' is then the third nitrogen atom).

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