Variable Temperature IR Spectroelectrochemical Investigation of the Stability of the Metal–Metal-Bonded Radical Anions $[(CO)_5MnRe(CO)_3(L)]^{\bullet-}$ (L = 2,2′-Bipyridine (BPY), 2,2′-Bipyrimidine (BPYM), 2,3-Bis(2-pyridyl)pyrazine (DPP)) and $[(CO)_5MnRe(CO)_3(L)Re(Br)(CO)_3]^{\bullet-}$ (L = BPYM, DPP) Controlled by the Lowest π^* (α-Diimine) Orbital Energy

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Cyclic voltammetry in combination with IR thin-layer spectroelectrochemistry was employed for detection and characterization of the radical anionic complexes $[(CO)_5MnRe(CO)_3(L)]^{\bullet-}$ (L = 2,2′-bipyridine (BPY), 2,2′-bipyrimidine (BPYM), and 2,3-bis-(2-pyridyl)pyrazine (DPP)) and $[(CO)_5MnRe(CO)_3(\mu\text{-L})Re(Br)(CO)_3]^{\bullet-}$ (μ-L = μ-BPYM, μ-DPP) as the primary products formed upon one-electron reduction of the neutral parent compounds. The stability of the radical anions is determined by the degree of polarization of the Mn–Re bond which increases in the order Mn–Re(μ-BPYM)Re < Mn–Re(μ-DPP)Re < Mn–Re(BPYM) ~ Mn–Re(DPP) < Mn–Re(BPY), i.e., with increasing energy of the π^* LUMO of the α-diimine ligand in the parent complexes and with increasing σ- and π-donor character of the α-diimine anion in the reduced species. In the same order, the unpaired electron in the metal–metal-bonded radical anions becomes more delocalized over the (Mn)Re–L chelate bond. This delocalization in turn also considerably destabilizes the d_{z^2} orbital of Re(L) involved in the Mn–Re bonding, making its occupation no more energetically convenient. Consequently, the Mn–Re bond will split heterolytically to give $[Mn(CO)_5]^-$ and $[Re(CO)_3(L)]^{\bullet}$. The trinuclear radical anion with μ-L = μ-BPYM was found to be stable already at room temperature and could be characterized also by UV–vis and ESR spectroscopy. The related radical anion with μ-DPP could only be stabilized at properly low temperatures, just as for the compounds with nonbridging BPYM and DPP. In the case of the BPY compound, the metal–metal-bonded radical anion could not be detected at all. Descriptions of the secondary reaction pathways of the radicals $[Re(CO)_3(L)]^{\bullet}$, formed in the course of the irreversible reduction of the above Mn–Re-bonded complexes, are given as well.

Introduction

It is a well-established fact that metal–metal-bonded complexes with the lowest unoccupied molecular orbital (LUMO) of a σ^*(M–M) character are prone to cleavage of the metal–metal bond upon reduction. In the absence of a bridging ligand, both metal centers are usually reduced in a direct two-electron step, and the only observable products are negatively charged fragments. Thus no evidence has so far been obtained for the existence of the radical anionic complexes $[M_2(CO)_{10}]^{\bullet-}$ (M = Mn, Re). The only product detected by cyclic voltammetry and spectroelectrochemistry in the course of the 2e reduction of parent $Mn_2(CO)_{10}$ is $[Mn(CO)_5]^-$ which may be reoxidized at a considerably more positive potential to give back $Mn_2(CO)_{10}$.[1–4]

The W–W-bonded dimer $[W_2(SBz)_2(CO)_8]$ (SBz = μ-phenylmethanethiolate) also undergoes 2e reduction localized on the σ^*(W–W) orbital.[5] However, due to the presence of the two bridging SBz ligands, it was still possible to distinguish between the individual 1e reduction steps. As a result, the primary reduction product, $[W_2(SBz)_2(CO)_8]^{\bullet-}$, could even be detected by IR spectroelectrochemistry.[5b] However, it was generated only in a very low concentration corresponding to a large value of the disproportionation constant described by eq 1. Consequently, it could not be established whether the radical anion still possesses an intact W–W bond or whether it contains the $W(CO)_4$ units linked only by the bridging SBz ligands, as was found in the final reduction product $[W_2(SBz)_2(CO)_8]^{2-}$.[5]

$$K_{disp} = \{[W_2(SBz)_2(CO)_8]^{2-}\}\cdot\{[W_2(SBz)_2(CO)_8]\}/\{[W_2(SBz)_2(CO)_8]^{\bullet-}\}^2 = 7500 \quad (1)$$

Opening of a metal–metal bond as a consequence of the population of the σ^*(M–M) LUMO also accompanies

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one-electron reduction of the cluster $Ru_3(CO)_{12}$. In this case the overall mechanism is more complex. The primary reduction product, $[Ru_3(CO)_{12}]^{\bullet-}$, is a very short-lived species which transforms to an open-structure isomer prone to dissociation of a CO ligand. Finally, the stable cluster, $[Ru_3(CO)_{11}]^{2-}$, with a CO-bridged triangular metal core is formed.[6]

From the above-mentioned examples it is apparent that stabilization of such radical anionic metal–metal-bonded complexes will require the presence of another redox active center (ligand) which is able to accommodate the unpaired electron in its low-lying LUMO, thus bypassing the labilizing effect of population of the σ^*(M–M) orbital at a higher energy.

Van der Graaf et al.[7] studied reduction of several $[(CO)_5MnMn(CO)_3(\alpha\text{-diimine})]$ complexes (α-diimine = a series of substituted 2,2′-bipyridine, 1,4-diaza-1,3-butadiene, and pyridine-2-carbaldehyde imine ligands). Coordination of an α-diimine ligand will have a stabilizing influence on the metal–metal bond in the singly reduced species since the SOMO is then the lowest π^* orbital of the α-diimine and not σ^*(M–M). Furthermore, the presence of an α-diimine ligand also results in sufficient separation between the first and second one-electron reduction steps. However, the primary radical anionic products, formed during the one-electron reduction of the above-mentioned complexes, have never been observed spectroscopically, not even in the case of the related compound $[(CO)_5MnRe(CO)_3(BPY')]$ (BPY′ = 4,4′-dimethyl-2,2′-bipyridine) with the more stable Mn–Re bond.[8] Instead, the metal–metal bond was instantaneously split with formation of $Mn(CO)_5^-$ and $[Mn(CO)_3(\alpha\text{-diimine})]^\bullet$ radicals. The latter species quickly dimerized to give $[Mn_2(CO)_6(\alpha\text{-diimine})_2]$. Likewise, one-electron reduction of $[(CO)_5MnRu(Me)(CO)_2(i\text{-Pr-DAB})]$ (i-Pr-DAB = *N,N′*-diisopropyl-1,4-diaza-1,3-butadiene) at 193 K yielded directly $Mn(CO)_5^-$ and the radical species $[Ru(Me)(n\text{-PrCN})(CO)_2(i\text{-Pr-DAB})]^\bullet$. The radical anion $[(CO)_5MnRu(Me)(CO)_2(i\text{-Pr-DAB})]^{\bullet-}$ was not even observed in traces.[9] The instantaneous fragmentation of the above reduced α-diimine complexes is very similar to the release of Br^- from the radical anions $[Re(Br)(CO)_3(\alpha\text{-diimine})]^{\bullet-}$.[10,11]

In order to find out if variation of the π^*(α-diimine) LUMO energy is responsible for differences in the stability of the metal–metal bond upon reduction, complexes of the type $[(CO)_5MnRe(CO)_3(L)]$ (L = 2,2′-bipyridine [BPY], 2,2′-bipyrimidine [BPYM], and 2,3-bis(2-pyridyl)pyrazine [DPP]) and $[(CO)_5MnRe(CO)_3(\mu\text{-L})Re(Br)(CO)_3]$ (μ-L = μ-BPYM, μ-DPP) were selected for this spectroelectrochemical study. The general structures of the complexes and the α-diimine ligands are depicted in Figure 1. In particular, the complexes

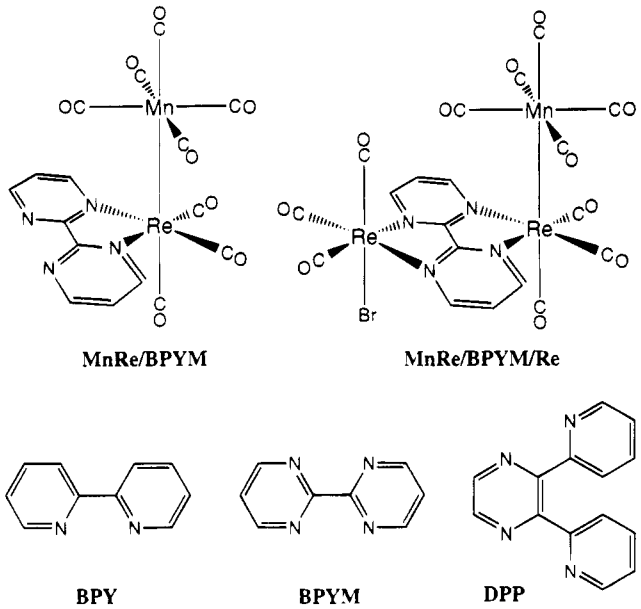

Figure 1. Molecular structures of the complexes MnRe/BPYM and MnRe/BPYM/Re and the α-diimine ligands L used.

with the bridging BPYM and DPP ligands were supposed to be good candidates for the reversible 1e reduction as the π^* LUMO of these ligands is known to be very low-lying.[12–14] In the text below the abbreviated formulas MnRe/L and MnRe/L/Re denote the dinuclear complexes $[(CO)_5MnRe(CO)_3(L)]$ and the trinuclear complexes $[(CO)_5MnRe(CO)_3(\mu\text{-L})Re(Br)(CO)_3]$, respectively.

Experimental Section

Materials and Preparations. Tetrahydrofuran (THF, Janssen Chimica) and butyronitrile (n-PrCN, Fluka) were distilled prior to use from a Na/benzophenone mixture and from CaH_2, respectively. The supporting electrolyte, Bu_4NPF_6 (Fluka), was dried overnight under vacuum at 80 °C. $Co(Cp)_2$ (Aldrich), Ferrocene (Fc, BDH), BPY (Merck), DPP (Aldrich), BPYM (Johnson & Matthey), Ag^+Otf^- (Otf^- = $CF_3SO_3^-$, Aldrich) were used as received.

The complexes MnRe/L (L = BPY, BPYM, DPP)[15,16] and MnRe/L/Re (L = BPYM, DPP)[17] were synthesized according to literature procedures and purified by column chromatography on Silica 60 (Merck), activated by heating overnight under vacuum at 180 °C, with gradient elution by n-hexane/THF. The complexes $[Re(X)(CO)_3(L)]$ (X = Cl^-, L = BPY;[18] X = Br^-, L = BPYM[19]) were prepared as reported in the literature. The complexes $[Re(Otf)(CO)_3(L)]$ (L = BPY, BPYM) were synthesized as previously described,[20] except for Ag^+Otf^- which was used as a reactant instead of H^+Otf^-.

All electrochemical and spectroelectrochemical samples were degassed by several freeze–pump–thaw cycles and handled

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carefully under a nitrogen atmosphere. The solutions of the light-sensitive di- and trinuclear complexes were prepared in the dark.

Spectroscopic Measurements and Instrumentation. IR spectra were measured on a BioRad FTS-7 FTIR spectrometer (16 scans, resolution of 2 cm^{-1}). Electronic absorption spectra were recorded on a Perkin Elmer Lambda 5 UV–vis spectrophotometer attached to a 3600 data station. An OTTLE cell,[2] equipped with a Pt minigrid working electrode (32 wires/cm) was used for IR and UV–vis spectroelectrochemical experiments at room temperature. Spectroelectrochemistry at low temperatures (LT) was performed in a home-made cryostated OTTLE cell, which has been described in detail elsewhere.[21] Quartz/CaF_2 and NaCl/CaF_2 windows were employed for UV–vis and IR OTTLE measurements, respectively. The working electrode surroundings were masked carefully to avoid passing the spectral beam through the nonelectrolyzed solution. Cyclic voltammetry and controlled potential electrolysis within the OTTLE cells were carried out by using PAR model 174 and PA4 (Ekom, Czech Republic) potentiostats. For all spectroelectrochemical samples the concentrations of the complexes and Bu_4NPF_6 were 5×10^{-3} and 4×10^{-1} M, respectively. Cyclic voltammograms were recorded at 293 and 213 K under the following conditions: 5×10^{-4} M redox active compound in n-PrCN or THF in the presence of 10^{-1} M Bu_4NPF_6, Pt disk electrode of 0.38 mm^2 area, Pt gauze auxiliary electrode, Ag wire pseudoreference electrode, a ligth-protected CV cell. All potentials are reported with respect to the ferrocene/ferrocenium (Fc/Fc^+) standard redox couple.[22]

Results

The MnRe/L and MnRe/L/Re complexes are reduced with one electron to give the corresponding radical anions which are stable or undergo secondary chemical reactions. In the latter case, a complete description of the reduction pathways of the metal–metal-bonded species also required spectroelectrochemical investigation of selected mononuclear complexes $[Re(X)(CO)_3(\alpha\text{-diimine})]$ (X = Cl^-, Br^-, Otf^-) (vide infra).

The ν(CO) frequencies of all complexes studied are collected in Table 1. The reduction potentials of the compounds are presented in Table 2.[23]

Cyclic Voltammetry. The reduction of MnRe/BPYM/Re at $E_{p,c} = -0.87$ V is apparently electrochemically ($\Delta E_p = 80$ mV vs 80 mV for Fc/Fc^+ at $v = 100$ mV/s; $E_{p,c}$ is independent of scan rate) as well as chemically ($I_{p,a}/I_{p,c} = 1$) reversible at room temperature on the cyclic voltammetry (CV) time scale. This reduction step is diffusion-controlled, as $I_{p,c}$ varies linearly with the square root of the scan rate in the range $10 < v < 500$ mV/s. Comparison with the reversible oxidation of ferrocene, present in the solution in equimolar concentration, revealed that the reduction of MnRe/BPYM/Re is a one-electron process. This result also agrees with the spectroelectrochemical reduction of MnRe/BPYM/Re (vide infra).

A peak showed up at $E_{p,a} = -0.64$ V during the anodic sweep after passing through the chemically irreversible reduction of $[MnRe/BPYM/Re]^{\bullet-}$ at $E_{p,c} = -1.50$ V. This peak can reasonably be assigned to reoxidation of $[Mn(CO)_5]^-$.[3,4] This observation points to inherent instability of the dianion $[MnRe/BPYM/Re]^{2-}$.

All the other Mn–Re-bonded complexes under study also showed diffusion-controlled, electrochemically reversible one-electron reduction. The reduction of MnRe/DPP/Re was chemically reversible on the time scale of cyclic voltammetry ($v = 20$–500 mV/s) already at room temperature, whereas the dinuclear complexes MnRe/

Table 1. CO-Stretching Frequencies of MnRe/L and MnRe/L/Re and Their Reduction Products in n-PrCN (Unless Stated Otherwise)

compd	ν(CO) (cm^{-1})
MnRe/BPY[a]	2055 m, 1997 s, 1948 vs, 1899 sh, 1890 m
$[Re(n\text{-}PrCN)(CO)_3(BPY)]^+$ [b]	2039 s, 1936 s, br
$[Re(n\text{-}PrCN)(CO)_3(BPY)]^\bullet$ [b]	2010 s, 1905 s, 1885 s
$[Re(CO)_3(BPY)]^-$ [a]	1944 s, 1843 s, br
$[Re(n\text{-}PrCN)(CO)_3(BPY)]^-$ [a]	1980 s, 1861 s, 1851 s
$[Re(Cl)(CO)_3(BPY)]$[c]	2021 s, 1916 m, 1897 m
$[Re(Cl)(CO)_3(BPY)]^{\bullet-}$ [c]	1996 s, 1881 m, 1865 m
MnRe/BPYM/Re[b]	2059 m, 2029 s, 2005 s, 1959 s, br, 1930 m, sh, 1917 s
$[MnRe/BPYM/Re]^{\bullet-}$ [b]	2050 m, 2016 s, 1996 s, br, 1939 s, br, 1910 m, 1896 s
MnRe/BPYM[c]	2056 m, 2001 s, 1949 vs, 1901 m
$[MnRe/BPYM]^{\bullet-}$ [c]	2044 m, 1985 s, 1939 s, br, 1864 m
$[Re(OTf)(CO)_3(BPYM)]$[b,d]	2040 s, 1934 s, br
$[Re(THF)(CO)_3(BPYM)]^+$ [b,d]	2026 s, 1941 s, 1915 s
$[Re(THF)(CO)_3(BPYM)]^\bullet$ [b,d]	2012 s, 1914 s, 1893 s
$[Re(Br)(CO)_3(BPYM)]^{\bullet-}$ [b]	2004 s, 1897 m, 1877 m
$[Re(THF)(CO)_3(BPYM)]^-$ [b,d]	1992 s, 1874 s, 1862 s
$[Re(n\text{-}PrCN)(CO)_3(BPYM)]^-$ [c]	1987 s, 1873 s, 1864 s
MnRe/DPP/Re[c]	2057 m, 2024 s, 2001 s, 1957 m, 1924 m, 1909 m
$[MnRe/DPP/Re]^{\bullet-}$ [c]	2049 m, 2007 s, 1991 s, 1943 s, br, 1897 sh, 1885 m
MnRe/DPP[a]	2055 m, 2000 s, 1952 vs, 1901 m
$[MnRe/DPP]^{\bullet-}$ [a]	2043 m, 1984 s, 1935 s, br, 1864 m
$[(Re(Br)(CO)_3)_2(\mu\text{-DPP})]$[b]	2022 s, 1920 s, br
$[Re(n\text{-}PrCN)(CO)_3(\mu\text{-DPP})\text{-}Re(Br)(CO)_3]^\bullet$ [b]	2012 sh, 2004 s, 1903 s, 1890 s
$[Mn(CO)_5]^-$	1902 s, 1862 s

[a] Measured at 183 K. [b] Measured at 293 K. [c] Measured at 213 K. [d] Measured in THF.

Table 2. Reduction Potentials (V vs Fc/Fc^+) of the Complexes MnRe/L, MnRe/L/Re, and Selected $[Re(X)(CO)_3(L)]^{0/-}$ (X = Halide, Solvent; L = BPY, BPYM) (5×10^{-4} M Bu_4NPF_6/n-PrCN Solution (v = 100 mV/s, Pt Disk Electrode)

compd	$E_{p,c}$[g]	(ΔE_p)	(ΔE_p) of Fc/Fc^+
MnRe/BPY	−1.73 (irr)[a]		
	−1.79 (irr)[b]	(111)	(85)
MnRe/BPYM	−1.53 (irr)[a]		
	−1.49 (rev)[b]	(115)	(115)
MnRe/DPP	−1.48 (irr)[a]		
	−1.46 (rev)[b]	(85)	(85)
MnRe/BPYM/Re	−0.87 (rev)[a]	(80)	(80)
	−0.87 (rev)[b]	(110)	(95)
MnRe/DPP/Re	−1.04 (rev)[a]	(115)	(115)
	−1.07 (rev)[b]	(190)	(160)
$[(Re(Br)(CO)_3)_2(\mu\text{-DPP})]$	−0.98 (rev)[a]	(65)	(65)
$[Re(Br)(CO)_3(BPYM)]$[e]	−1.42 (rev)[a,d]	(80)	
$[Re(THF)(CO)_3(BPYM)]^+$	−1.28 (rev)[a]	(85)	(85)
$[Re(Br)(CO)_3(BPYM)]^{\bullet-}$ [e]	−2.04 (irr)[a,d]		
$[Re(THF)(CO)_3(BPYM)]^\bullet$	−1.73 (rev)[a]		
$[Re(Cl)(CO)_3(BPY)]$[f]	−1.91 (rev)[a,c]	(110)	
$[Re(Cl)(CO)_3(BPY)]^{\bullet-}$ [f]	−2.38 (irr)[a,c]		
$[Re(n\text{-}PrCN)(CO)_3(BPY)]^+$	−1.62 (rev)[a]	(100)	(100)
$[Re(n\text{-}PrCN)(CO)_3(BPY)]^\bullet$	−1.97 (irr)[a]		

[a] Measured at 293 K. [b] Measured at 213 K. [c] Measured in THF. [d] Measured in DMF. [e] See ref 11. [f] See ref 10. [g] Chemical reversibility (rev)/irreversibility (irr) indicated in brackets.

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(23) Electrochemical reversibility of all investigated electrode processess was compared with that of the Fc/Fc^- couple[22] used as an internal standard to account for effects such as uncompensated *iR* drop, electrode passivation, etc.

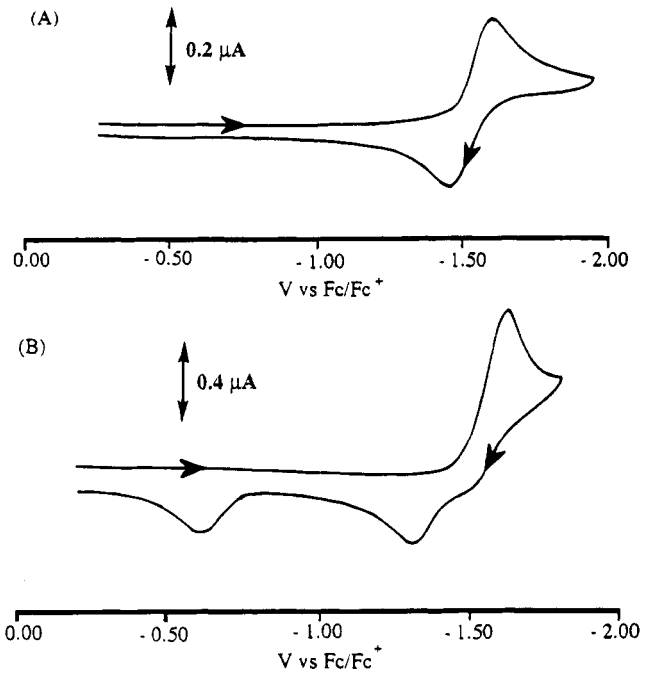

Figure 2. Cyclic voltammograms of MnRe/BPYM measured in n-PrCN at 213 K (A) and 293 K (B). Conditions: 5 × 10^{-4} M solution in n-PrCN in the presence of 10^{-1} M Bu_4NPF_6, Pt disk electrode (real surface area of 0.38 mm^2), v = 100 mV/sec.

BPYM (Figure 2A) and MnRe/DPP were reversibly reduced only at 213 K. At room temperature the reduction of the latter complexes was chemically irreversible ($I_{p,a}/I_{p,c}$ < 1) (Figure 2B). The reduction of MnRe/BPY was chemically irreversible even at 213 K. This irreversibility indicates that the primary reduction product $[MnRe/BPY]^{\bullet-}$ undergoes a very fast scission of the Mn–Re bond with a rather low activation energy which increases in the order MnRe/BPY < MnRe/L ≪ MnRe/L/Re (L = DPP, BPYM). For, the irreversible cathodic processes were associated in all MnRe/L cases with the appearance of two new anodic peaks on the reverse scan (see Figure 2B) due to reoxidation of the secondary products $Mn(CO)_5^-$ at $E_{p,a}$ = −0.6 V[3,4] and $[Re(n\text{-}PrCN)(CO)_3(L)]^{\bullet}$ at more negative potentials (see Table 2).

Spectroelectrochemistry. MnRe/BPYM/Re. Electrochemical reduction of MnRe/BPYM/Re in n-PrCN within the IR OTTLE cell at room temperature gave a product with bands in the ν(CO) region at 2050 m, 2016 s, 1996 s,br, 1939 s,br, 1910 m,sh, and 1896 s cm^{-1}. The band pattern is identical to that of the parent compound MnRe/BPYM/Re (Table 1, Figure 3), and the product is therefore assigned as the radical anionic complex $[MnRe/BPYM/Re]^{\bullet-}$. The shift of the ν(CO) bands to lower frequencies upon reduction of MnRe/BPYM/Re can obviously be ascribed to an increased π-back-donation from the metal centers toward the CO ligands. The magnitude of the ν(CO) shifts of ~15–20 cm^{-1} agrees with the expected value for α-diimine-localized one-electron reduction steps[10] and points to a weak π-donation from the bis-chelated $[BPYM]^{\bullet-}$ radical anionic ligand to both Re centers.

The radical anion $[MnRe/BPYM/Re]^{\bullet-}$ is stable at room temperature. It could also be obtained chemically by smooth reduction of MnRe/BPYM/Re with 1 equiv of $Co(Cp)_2$ in THF ($Co(Cp)_2/Co(Cp)_2^+$ possesses $E_{1/2}$ = −1.33 V vs Fc/Fc^+). In this way it was possible to characterize $[MnRe/BPYM/Re]^{\bullet-}$ by ESR (Figure 4) and UV–vis spectroscopy (Figure 5).

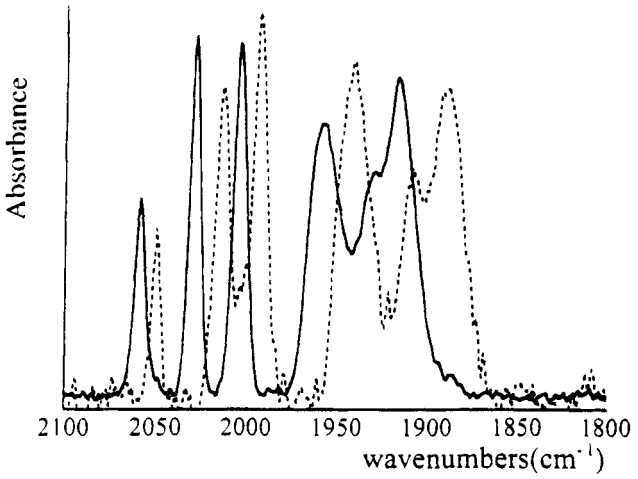

Figure 3. IR spectra of MnRe/BPYM/Re (—) and $[MnRe/BPYM/Re]^{\bullet-}$ (···) in the ν(CO) region; in n-PrCN at 293 K.

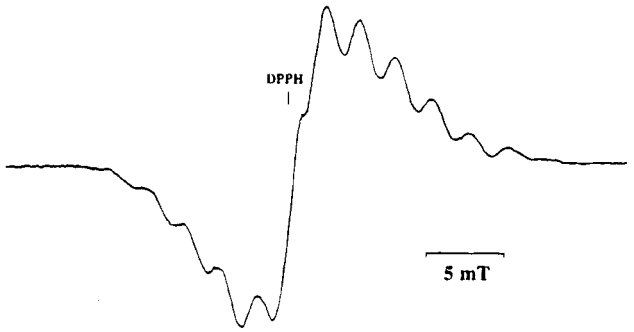

Figure 4. ESR spectrum of $[MnRe/BPYM/Re]^{\bullet-}$ in THF at 293 K.

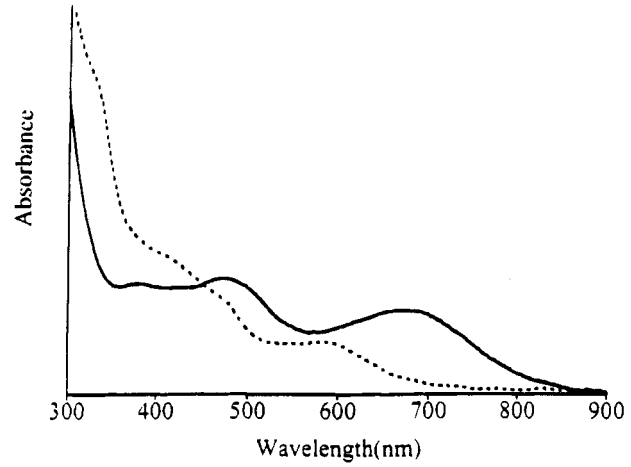

Figure 5. 5. UV–vis spectra of MnRe/BPYM/Re (—) and $[MnRe/BPYM/Re]^{\bullet-}$ (···) in n-PrCN at 293 K.

The radical anion $[MnRe/BPYM/Re]^{\bullet-}$ exhibits a partially resolved ESR spectrum at g = 1.9990 (Figure 4). The spectrum has apparently an asymmetric shape which may be ascribed to second-order effects (deviations in spacing between lines and in line width) due to insufficient averaging of anisotropic contributions (g factors, splitting constants), not uncommon for the coupling from the $^{185,187}Re$ nuclei.[24] This feature in combination with possible hyperfine splitting due to the large number of nuclei (two inequivalent ^{185}Re (I = $^5/_2$, 37.07%) or ^{187}Re (I = $^5/_2$, 62.93%) nuclei, one ^{55}Mn

nucleus ($I = {}^5/_2$), one ^{79}Br ($I = {}^3/_2$, 50.54%) or ^{81}Br ($I = {}^3/_2$, 49.46%) nucleus, four ^{14}N ($I = 1$, 99.63%) and two (of six)[25] ^1H ($I = {}^1/_2$, 100%) nuclei of the BPYM heterocycle) make the computer simulation of the ESR spectrum rather difficult. The best result has been obtained with the following parameters: the coupling constants $a_{Re(Mn)} = a_{Re(Br)} = 2.4$ mT (sextets of the line-intensity pattern 1:2:3:3:2:1), $a_{Mn} = a_{Br} = 0.9$ mT, line width of 1.4 mT. For comparison, the ESR spectrum of the related BPYM-centered radical anion $[(Re(Br)(CO)_3)_2(\mu\text{-BPYM})]^{\bullet-}$ has been recorded[26] at $g = 2.0005$, and the computer simulation inferred $a_{Re} = 1.2$ mT and $a_{Br} = 0.8$ mT. The rhenium coupling constant (a_{Re}) of approximately 2.4 mT for $[MnRe/BPYM/Re]^{\bullet-}$ clearly indicates that this radical anion is also BPYM-centered since a rhenium-centered radical would possess much larger a_{Re} ($\geq$20 mT).[24,27] The relatively small isotropic g factor of $[MnRe/BPYM/Re]^{\bullet-}$ (see above) with respect to the value $g_e = 2.0023$ of the free electron reflects mixing of the singly occupied MO (SOMO) of the $[BPYM]^{\bullet-}$ ligand, b_{2u}^*,[25] with a low-lying unoccupied MO (which might be[25] the a_u^* LUMO of $[BPYM]^{\bullet-}$) through the spin–orbit coupling[28] due to the presence of the heavy Re atoms.

The UV–vis spectrum of MnRe/BPYM/Re (Figure 5) shows two MLCT transitions at 473 and 671 nm in THF. A resonance Raman study on this complex[17] revealed that the lower-energy MLCT band originates from the (Mn)Re metal center whereas the higher-energy MLCT transitions originate mainly from the Re(Br) metal center. Upon the one-electron reduction the lowest energy band shifts approximately 2600 cm^{-1} to higher energy. Provided that the SOMO of $[MnRe/BPYM/Re]^{\bullet-}$ still has π^*(BPYM) character, which is indicated by ESR spectroscopy (vide supra) and the stability of the radical, this shift of the MLCT band may be ascribed to a larger destabilization of the π^*(BPM) frontier orbital upon single occupation with respect to the filled d_π(Re(Mn)) orbitals.

Further reduction of $[MnRe/BPYM/Re]^{\bullet-}$ ($E_{p,c} = -1.50$ V vs Fc/Fc^+) led to instantaneous splitting of the Mn–Re bond, as was indicated by the appearance of the characteristic ν(CO) bands of $Mn(CO)_5^-$ accompanied by the generation of yet unidentified product(s) (ν(CO) at 2018 s, 1932 s, and 1915 s cm^{-1}).

MnRe/DPP/Re. At room temperature, $[MnRe/DPP/Re]^{\bullet-}$ was not as stable on the OTTLE time scale of minutes as $[MnRe/BPYM/Re]^{\bullet-}$ since it slowly decomposed into $Mn(CO)_5^-$ and a product with ν(CO) bands at 2012 sh, 2004 s, 1903 s, and 1890 s cm^{-1}. The latter frequencies are tentatively assigned to $[Re(n\text{-}PrCN)(CO)_3(\mu\text{-DPP})Re(Br)(CO)_3]^{\bullet}$. A product with the same ν(CO) frequencies is formed upon one-electron reduction of $[(Re(Br)(CO)_3)_2(\mu\text{-DPP})]$.[29,30] At 213 K, however, the one-electron reduction of MnRe/DPP/Re was also completely reversible on the OTTLE time scale. This was indicated by the isosbestic appearance of the ν(CO) bands of $[MnRe/DPP/Re]^{\bullet-}$ (Table 1) which persisted in the solution at the reduced temperature for more than 10 min without any apparent decomposition. Only further reduction of the radical anion at $E_{p,c} = -1.50$ V vs Fc/Fc^+ led again to the formation of $Mn(CO)_5^-$ and some unidentified products with ν(CO) at 2031 (sh), 2026, 2011, and 1906 (broad) cm^{-1}.

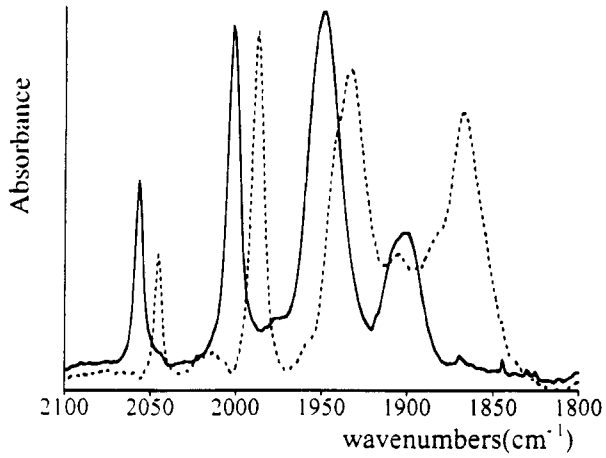

Figure 6. IR spectra of MnRe/BPYM (—) and $[MnRe/BPYM]^{\bullet-}$ (···) in the ν(CO) region; in n-PrCN at 193 K.

MnRe/BPYM. Figure 6 shows the IR spectral changes in the ν(CO) region accompanying the reduction of MnRe/BPYM in n-PrCN at 213 K. Using the same reasoning as for $[MnRe/BPYM/Re]^{\bullet-}$ (vide supra) the product formed is assigned to the radical anion $[MnRe/BPYM]^{\bullet-}$ (Table 1). Although stable on the CV time scale (v = 20–500 mV/s) at 213 K, $[MnRe/BPYM]^{\bullet-}$ slowly decomposed during electrolysis within the LT OTTLE cell into $Mn(CO)_5^-$ and $[Re(n\text{-}PrCN)(CO)_3(BPYM)]^{\bullet}$. The latter product could not, however, be observed spectroscopically since it was immediately reduced further to give $[Re(n\text{-}PrCN)(CO)_3(BPYM)]^-$. The identity of the latter product was confirmed by independent reduction of $[Re(Otf)(CO)_3(BPYM)]$ in THF and of $[Re(Br)(CO)_3(BPYM)]$ in n-PrCN (see Scheme 1).

$[Re(Otf)(CO)_3(BPYM)]$ was completely converted prior to its one-electron reduction in THF to $[Re(THF)(CO)_3(BPYM)]^+$. For the description of the mechanism of this electrocatalyzed substitution we refer to previous works of Kochi et al.[31] and Stor et al.[10] Subsequent one-electron reduction of the latter cationic compound gave smoothly the radical complex $[Re(THF)(CO)_3(BPYM)]^{\bullet}$. In a subsequent one-electron reduction step this radical was converted into $[Re(THF)(CO)_3(BPYM)]^-$ upon retention of isosbestic points in the IR ν(CO) region. Importantly, the ν(CO) frequencies of $[Re(THF)(CO)_3(BPYM)]^-$ strongly resemble those of the final Re product formed upon reduction of MnRe/BPYM in n-PrCN (see Scheme 1), thus proving its assignment to $[Re(n\text{-}PrCN)(CO)_3(BPYM)]^-$ (Table 1).

The anion $[Re(n\text{-}PrCN)(CO)_3(BPYM)]^-$ was also spectroelectrochemically generated by stepwise reduction of $[Re(Br)(CO)_3(BPYM)]$ in n-PrCN at room temperature. The first one-electron reduction step led to the formation of stable $[Re(Br)(CO)_3(BPYM)]^{\bullet-}$. Its subsequent one-

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(29) The uptake of one electron probably leads to a heterolytic splitting of only one of the Re–Br bonds and a concomitant replacement of Br^- by a donor solvent molecule, as was indicated by a different ν(CO) pattern of the asymmetric radical product with respect to that found for parent $[(Re(Br)(CO)_3)_2(\mu\text{-DPP})]$ (see Table 1).
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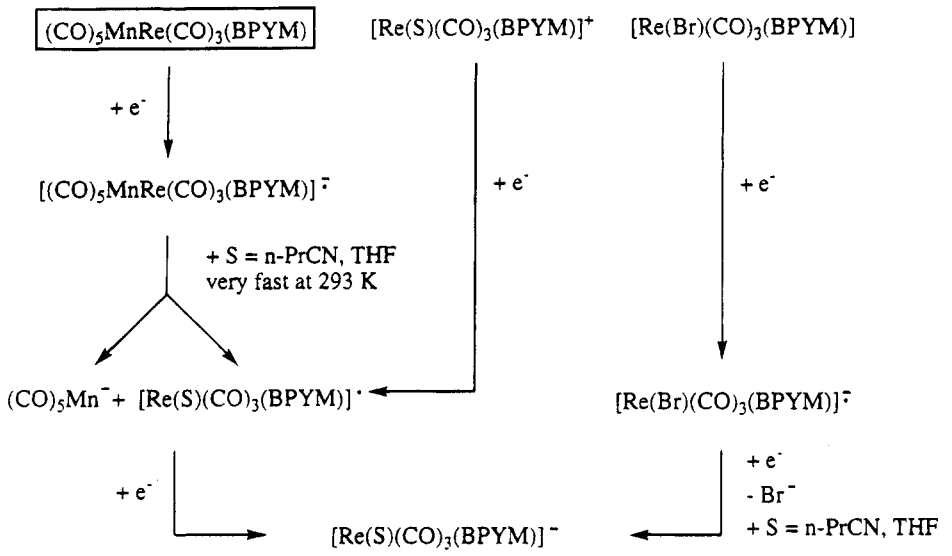
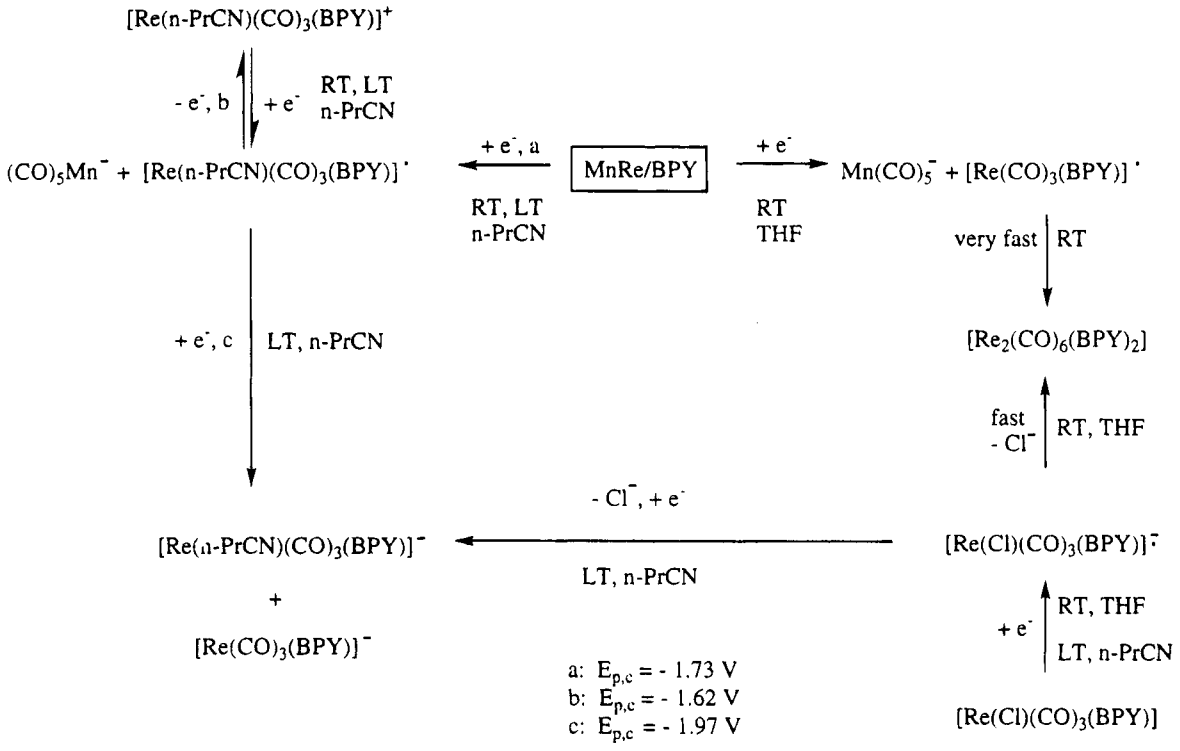
Scheme 1



Scheme 2



electron reduction concomitantly gave $[Re(n\text{-}PrCN)(CO)_3(BPYM)]^-$ owing to fast dissociation of the bromide ligand.

The unequivocal assignment of the above mononuclear reduction products was also facilitated by close correspondence between the reduction pathways of $[Re(X)(CO)_3(BPYM)]$ under study and those of related $[Re(X)(CO)_3(APY)]$ (APY = azo-2,2′-pyridine, X = Otf^-, Br^-) in THF.[10]

MnRe/DPP. The radical anionic species $[MnRe/DPP]^{\bullet-}$ could only be generated in a spectroscopically detectable amount by performing the reduction of MnRe/DPP at 183 K (Table 1). Even at that temperature a rapid decomposition was observed in the course of the reduction, producing again $[Mn(CO)_5]^-$ and a species with ν(CO) bands at 2002 and 1944 cm^{-1}.

MnRe/BPY. The virtually irreversible character of the reduction of MnRe/BPY, as was revealed by cyclic voltammetry (vide supra), has further been confirmed by IR spectroelectrochemistry in n-PrCN at 183 K. This experiment indeed showed instantaneous formation of $Mn(CO)_5^-$ together with the radical $[Re(n\text{-}PrCN)(CO)_3(BPY)]^\bullet$. The latter product was partly reoxidized at the applied potential of the minigrid working electrode to the cation $[Re(n\text{-}PrCN)(CO)_3(BPY)]^+$ (see Scheme 2). Further reduction of $[Re(n\text{-}PrCN)(CO)_3(BPY)]^\bullet$ led to the formation of both hexacoordinated $[Re(n\text{-}PrCN)(CO)_3(BPY)]^-$ and pentacoordinated $[Re(CO)_3(BPY)]^-$. It is noteworthy that no traces of the primary reduction product $[MnRe/BPY]^{\bullet-}$ were even observed at 183 K.

At room temperature, the product of the irreversible one-electron reduction of MnRe/BPY depends on the solvent used. In THF, formation of the dimeric species $[Re_2(CO)_6(BPY)_2]$ out of $[Re(CO)_3(BPY)]^\bullet$ was evidenced

by IR and UV–vis spectra (ν(CO) at 1988 s, 1951 s, 1887 s, and 1859 s cm^{-1}; λ_{max} 805, 600, and 470 nm).[10] In n-PrCN at room temperature, however, formation of the dimer $[Re_2(CO)_6(BPY)_2]$ was not observed. Instead, one-electron reduction of MnRe/BPY led to the formation of $Mn(CO)_5^-$ and $[Re(n\text{-}PrCN)(CO)_3(BPY)]^+$ (see Scheme 2).

The assignment of the above Re/BPY products was supported by the results of independent spectroelectrochemical reduction of $[Re(Otf)(CO)_3(BPY)]$ in n-PrCN at room temperature and $[Re(Cl)(CO)_3(BPY)]$ in n-PrCN at 213 K. $[Re(Otf)(CO)_3(BPY)]$ immediately converted in n-PrCN at room temperature into $[Re(n\text{-}PrCN)(CO)_3(BPY)]^+$. The one-electron reduction of the latter species gave the stable radical $[Re(n\text{-}PrCN)(CO)_3(BPY)]^\bullet$ as the only product. The one-electron reduction of $[Re(Cl)(CO)_3(BPY)]$ at 213 K in n-PrCN resulted in the formation of the stable radical anion $[Re(Cl)(CO)_3(BPY)]^{\bullet-}$. $[Re(Cl)(CO)_3(BPY)]^{\bullet-}$ was further reduced to give a product with ν(CO) bands at 1980 s, 1861 s, and 1851 s cm^{-1} and a minor amount of a product with ν(CO) bands at 1944 s and 1843 s, br cm^{-1}. The ν(CO) frequencies of the former product strongly resemble those of $[Re(n\text{-}PrCN)(CO)_3(DAPA)]^-$ (DAPA = 2,6-diacetylpyridine bis(anil) (ν(CO) at 1980 s, 1856 s, and 1842 s cm^{-1})[10] and those of $[Re(n\text{-}PrCN)(CO)_3(BPYM)]^-$ (Table 1). The complex is therefore assigned to $[Re(n\text{-}PrCN)(CO)_3(BPY)]^-$. The latter product corresponds to pentacoordinated $[Re(CO)_3(BPY)]^-$, in accordance with the results of Stor et al.[10] Scheme 2 summarizes the various events taking place upon reduction of MnRe/BPY, $[Re(Cl)(CO)_3(BPY)]$, and $[Re(Otf)(CO)_3(BPY)]$.

Discussion

The (spectro)electrochemical data presented in the previous section clearly show that the cleavage of a metal–metal bond in transition metal complexes upon reduction may successfully be avoided by coordination of π-acceptor ligands which are able to accommodate the added electrons in their low-lying empty π^* orbitals. The α-diimine ligands proved to be suitable candidates for this strategy. It is noted that they posses a similar stabilizing effect for the Re–X bond in the complexes $[Re(X)(CO)_3(\alpha\text{-diimine})]^{\bullet-}$ (X = halide)[10] depending on their basicity in the singly reduced form.

A comparison of the reduction potentials of the complexes MnRe/α-diimine revealed that BPY ($E_{p,c}$(MnRe/BPY) = −1.73 V vs Fc/Fc^+ at 293 K) possesses the highest-energy π^* LUMO and has, therefore, the weakest π-acceptor character. BPYM and DPP in MnRe/L are comparable in their π-acceptor capacity ($E_{p,c}$(MnRe/BPYM) = −1.53 V vs Fc/Fc^+ at 293 K; $E_{p,c}$(MnRe/DPP) = −1.48 V vs Fc/Fc^+ at 293 K). Their π-acceptor character becomes much stronger in MnRe/L/Re where they act as bridges between the two Re central atoms ($E_{p,c}$(MnRe/BPYM/Re) = −0.87 V vs Fc/Fc^+ at 293 K; $E_{p,c}$(MnRe/DPP/Re) = −1.04 V vs Fc/Fc^+ at 293 K). The decrease of the π^* orbital energy of the bridging versus nonbridging BPYM or DPP is a well-known phenomenon[12–14] caused by coordination of a second electron-withdrawing metal center. The effect is also apparent from the UV–vis spectra of the di- and trinuclear BPYM and DPP compounds.[17] The d((Mn)Re) → π^*(BPYM) CT band of MnRe/BPYM at 523 nm (in THF, room temperature) shifts to 671 nm in MnRe/BPYM/Re and an extra MLCT band, originating mainly from the Re center of the $Re(Br)(CO)_3$ fragment, is observed at 473 nm for the trinuclear compound. The d_π((Mn)Re) → π^*(DPP) CT band at 557 nm shifts to 636 nm going from MnRe/DPP to MnRe/DPP/Re, and an extra MLCT band shows up at 474 nm for the latter compound due to the coordination of the $Re(Br)(CO)_3$ metal fragment.

The radical anion $[MnRe/BPYM/Re]^{\bullet-}$ is stable at room temperature, whereas the radical anion $[MnRe/DPP/Re]^{\bullet-}$ could only be stabilized at 213 K. This difference in reactivity implies that the bridging BPYM ligand offers a lower-lying π^* LUMO than bridging DPP and is, therefore, more suitable for accommodation of the extra electron. This is in accordance with the reduction potentials of the neutral compounds which are $E_{p,c}$ = −0.87 V and $E_{p,c}$ = −1.04 V for MnRe/BPYM/Re and MnRe/DPP/Re, respectively.

Considering the dinuclear species, the most stable radical anion is formed by the one-electron reduction of MnRe/BPYM. $[MnRe/BPYM]^{\bullet-}$ could already be stabilized at 213 K whereas for $[MnRe/DPP]^{\bullet-}$ the temperature had to be decreased to 183 K. This is rather surprising since the reduction potentials of MnRe/BPYM ($E_{p,c}$ = −1.53 V) and MnRe/DPP ($E_{p,c}$ = −1.48 V) are very similar. Apparently, other effects play a role. For the $[BPYM]^{\bullet-}$ ligand it is known from MO calculations[32] that the electron density on its π^* SOMO (b_{2u}^*) should be localized on the inter-ring C–C bond. Complexes with α-diimine ligands of the type $[R\text{–}DAB]^{\bullet-}$ (R = alkyl, aryl; DAB = 1,4-diaza-1,3-butadiene) are expected to have the electron density in their π^* SOMO delocalized over the C=N bonds.[33,34] Supposing this is also true for the $[DPP]^{\bullet-}$ ligand, the π^* electron will then be more delocalized over the (Mn)Re–DPP chelate bond than in the complex with the $[BPYM]^{\bullet-}$ ligand. Consequently, the increased electron density on the Re atom will result in stronger polarization and hence in more facile cleavage of the Mn–Re bond (see below).

$[MnRe/BPY]^{\bullet-}$ was not even observed at low temperatures since $[BPY]^{\bullet-}$ ($E_{p,c}$(MnRe/BPY) = −1.73 V vs Fc/Fc^+) is apparently a much stronger σ,π-donor in this case. This particular property of the BPY ligand was also demonstrated by several other authors.[9–11,35] For example, Stor et al.[10] reported a facile loss of Br^- from $[Re(Br)(CO)_3(BPY)]^{\bullet-}$ at room temperature whereas the related complexes with the $[DPP]^{\bullet-}$ and $[APY]^{\bullet-}$ ligands are inherently stable. In this respect we have shown in this study that the related $[Re(Cl)(CO)_3(BPY)]^{\bullet-}$ radical anions could in fact be stabilized by simply lowering the temperature to 213 K. This temperature was sufficiently low to inhibit completely the follow-up dissociation of the chloride ligand, even in the absence of excess Cl^- anions in the solution, which is otherwise required at room temperature.[36]

The above results illustrate that the heterolytic splitting of the Mn–Re bond in $[MnRe/L]^{\bullet-}$ and [MnRe/

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L/Re]$^{\bullet-}$ has its origin in a strong polarization of this bond by a charge "leakage" from the reduced α-diimine ligand. The basicity,[24] i.e., the σ- and π-donor character of the α-diimine radical anion, increases in the order [BPYM]$^{\bullet-}$ < [DPP]$^{\bullet-}$ < [BPY]$^{\bullet-}$. In the same order the unpaired electron becomes more delocalized over the Re−L chelate bond which will in turn considerably destabilize also the d_{z^2} orbital of Re involved in the Mn−Re σ-bonding. The doubly-occupied σ(Mn−Re) orbital will then also rise in energy and will obtain an increasing d_{z^2}(Mn) contribution. The Mn−Re bond will therefore be polarized to such an extent that it will split heterolytically into $Mn^{-}\cdots Re^{+}(L^{\bullet-})$, which has indeed been confirmed by the observed formation of $[Mn(CO)_5]^-$ and the reactive radicals $[Re(CO)_3(L)]^{\bullet}$ (see Schemes 1 and 2). The same mechanism of the σ-bond polarization probably applies also for the dissociation of Br^- from $[Re(Br)(CO)_3(L)]^{\bullet-}$.[10]

The strong influence of the increased basicity of the α-diimine ligand on the lability of a metal−metal bond can also be demonstrated by the formation of $[(CO)_5ReRe(CO)_3(L_2)]$ upon reaction of $[Re(CO)_5]^-$ with $[Re(Cl)(CO)_3(L_2)]$.[37] The Re−Re bond was formed for L_2 = BPY whereas no reaction was observed for the significantly more basic pyridine (PY) ligands ($E_{1/2}$(PY/PY$^{\bullet-}$) − $E_{1/2}$(BPY/BPY$^{\bullet-}$) = −690 mV[37]).

Conclusions

The radical anionic complexes [MnRe/L]$^{\bullet-}$ and [MnRe/L/Re]$^{\bullet-}$ can be stabilized by coordination of strong π-acceptor α-diimine ligands (L = BPYM, DPP) and by sufficiently decreasing the temperature. These compounds are the first radical−anionic metal−metal-bonded complexes of this type characterized spectroscopically.

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