Unusually Stable Radical Anionic Complexes [(CO)5MnRe(CO)3(BPM)]•−, [(CO)5MnRe(CO)3(BPM)Re(CO)3Br]•−, [Os3(CO)10(BPM)]•−, and [Os3(CO)10(BPM)Re(CO)3Br]•− (BPM = 2,2′-Bipyrimidine) Studied with Cyclic Voltammetry and IR Spectroelectrochemistry at Variable Temperatures

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Metal–metal-bonded complexes such as $Mn_2(CO)_{10}$, $Cp_2Fe_2(CO)_4$, or $Cp_2Mo_2(CO)_6$ possess a lowest empty $\sigma^*(M-M)$ orbital. Occupation of this orbital gives rise to prompt cleavage of the metal–metal bond.[1-4] Thus, no evidence has been obtained so far for the existence of the radical anionic complex $[Mn_2(CO)_{10}]^{\bullet-}$.[5] Similarly, $W_2(SBz)_2(CO)_8$ undergoes a chemically reversible 2e− reduction to give $[W_2(SBz)_2(CO)_8]^{2-}$ in which complexion the W–W bond is broken and the $W(CO)_4$ fragments remain connected by the two benzoyl mercaptide (SBz) ligands.[6]

Radical anionic carbonyl clusters of low nuclearity are also highly reactive in the absence of either stabilizing ligands such as carbides or a close-packed structure.[7] For example, one-electron reduction of $Ru_3(CO)_{12}$ is followed by opening of a Ru–Ru bond, loss of CO, and formation of triangular $[Ru_3(CO)_{11}]^{2-}$.[8] The same type of product is formed upon reduction of $Os_3(CO)_{12}$.[9] Substitution of two carbonyl ligands in a metal–metal-bonded complex by an α-diimine such as 2,2′-bipyridine will have a stabilizing influence on the metal–metal bond(s) of the anionic complex since the singly occupied molecular orbital (SOMO) is then the lowest π^* orbital of the α-diimine and not $\sigma^*(M-M)$. It has, however, been shown that electrochemical reduction of $(CO)_5MnMn(CO)_3(bpy)$[10] as well as $(CO)_5MnRu(Me)(CO)_2$-(*i*-Pr-PyCa)(Me = methyl; *i*-Pr-PyCa = *N*-isopropylpyridine-2-carbaldimine)[11] also leads to instantaneous formation of $[Mn(CO)_5]^-$. This result is not unexpected since both bpy and *i*-Pr-PyCa transform into rather strong donors upon reduction. It is also in line with the observation that $[Mn(CO)_3L]^+$ and $[Mn(CO)_5]^-$ only produce the metal–metal-bonded complex $(CO)_5MnMn(CO)_3L$ if L is a weak base such as an α-diimine ligand and not in the case of e.g. 1,2-bis(diphenylphosphino)-ethane.[12]

We wondered if stable metal–metal-bonded anionic complexes might be formed by further reducing the basic properties of the α-diimine or by lowering the temperature to such an extent that the barrier for the decomposition reaction could not be crossed anymore. Preliminary results obtained for the complexes $(CO)_5MnRe(CO)_3(BPM)$ (1), $(CO)_5MnRe(CO)_3(BPM)Re(CO)_3Br$ (2), $Os_3(CO)_{10}(BPM)$[13] (3), and $Os_3(CO)_{10}(BPM)Re(CO)_3Br$ (4) (BPM) = 2,2′-bipyridine) provide clear evidence that both ways can be successful.

Table 1. Reduction Potentials (V vs Fc/Fc+) of 10^{-4} M Solutions of the Complexes **1–4** in 3×10^{-1} M Bu_4NPF_6/n-PrCN at $v = 100$ mV/s with Pt Disk Electrode of 0.8 mm² Area

complex	$E_{1/2}^{I\ d}$	ΔE_p
$(CO)_5MnRe(CO)_3(BPM)^c$ (1)	−1.49^a	115^a
$(CO)_5MnRe(CO)_3(BPM)Re(CO)_3Br$ (2)	−0.87^{a,b}	110,^{a} 80^b
$Os_3(CO)_{10}(BPM)$ (3)	−1.44^b	70^b
$Os_3(CO)_{10}(BPM)Re(CO)_3Br$ (4)	−0.88^b	95^b

^{a} Measured at 213 K. ^{b} Measured at 293 K. ^{c} Irreversible reduction at $E_{p,c} = -1.53$ V at 293 K; anodic peaks of $[Re(CO)_3(BPM)(n-PrCN)]^\bullet$ and $[Mn(CO)_5]^-$ reoxidation observed in the cyclic voltammogram at the reverse scan at $E_{p,a} = -1.27$ and -0.59 V vs Fc/Fc+, respectively. ^{d} Potentials given vs Fc/Fc+ redox couple used as the internal standard.

The electrochemical reductions of the complexes were followed by cyclic voltammetry (CV) and FTIR spectroelectrochemistry at variable temperatures. The latter results were obtained by using a specially constructed cryostated optically transparent thin layer electrochemical (OTTLE) cell.[14]

After comparison of the reduction potentials of the complexes (Table 1), it is evident that the bridging BPM ligand has a stronger π-acceptor character than if this ligand coordinates to only one metal fragment, for the reduction potentials of **2** and **4** are clearly less negative than those of **1** and **3**. Cyclic voltammograms of complexes **2–4** show both electrochemically and chemically reversible 1e− reduction at 293 K.[15] For complex **1** such a behavior could only be obtained by lowering the temperature to 213 K. However, from the reversible behavior of **2–4** on the CV time scale, it may not be concluded that the primary reduction products do not undergo a structural change on a longer time scale. In this respect the IR spectroelectrochemical data are more informative. Retention of structure upon reduction was evident for **2**[16] and **4** from the IR spectral changes which showed a simple shift of all ν(CO) bands to lower frequencies while the intensity pattern did not change (Table 2; Figure 1). Reduction of **3** on the other hand finally produced a radical anion **3′**•− which had a structure different from that of the parent compound and from the shortly-lived primary reduction product **3**•− according to its IR spectrum (Table 2). In this case formation of **3′**•− was a partially reversible process at 293 K. The radical anions **3′**•− and **4**•−, derived from the Os-clusters **3** and **4**, respectively, differ in retention of the cluster structure in the case of **4**•− and cleavage of an Os–Os(BPM) bond upon reduction of **3**. It is noteworthy that a reversible opening and closing of the latter cluster can also be achieved photochemically.[17]

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(15) ΔE_p is identical with ΔE_p of the ferrocene/ferrocenium redox couple used as the internal standard; the peak current function is $i_p^a/i_p^c = 1$ for $v = 20$–200 mV/s.
(16) The inherent stability of **2**•− has been confirmed by smooth reduction of **2** with 1 equiv of $Co(Cp)_2$ ($Co(Cp)_2/Co(Cp)_2^+$ possesses $E_{1/2} = -1.33$ V vs Fc/Fc+). The product has an IR spectrum identical to that obtained spectroelectrochemically. It has been characterized also by ESR spectroscopy. Details will be reported in a forthcoming article.
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Table 2. CO-Stretching Frequencies of the Parent Complexes 1–4 and the Radical Anionic Products

complex	ν(CO), cm^{-1} [c]
(CO)$_5$MnRe(CO)$_3$(BPM)[a] (**1**)	2055 m, 2000 s, 1948 s, br, 1901 m
[(CO)$_5$MnRe(CO)$_3$(BPM)][•– a] (**1•–**)	2044 m, 1985 s, 1939 s, br, 1864 m
(CO)$_5$MnRe(CO)$_3$(BPM)Re(CO)$_3$Br[b] (**2**)	2059 m, 2029 s, 2005 s, 1959 s, br, 1930 m, sh, 1917 s
[(CO)$_5$MnRe(CO)$_3$(BPM)Re(CO)$_3$Br]•– b (**2•–**)	2050 m, 2016 s, 1996 s, 1939 s, br, 1910 m, sh, 1896 s
Os$_3$(CO)$_{10}$(BPM)Re(CO)$_3$Br[b] (**4**)	2092 m, 2045 m, 2029 s, 2004 s, br, 1988 sh, 1965 sh, 1932 m, 1918 m
[Os$_3$(CO)$_{10}$(BPM)Re(CO)$_3$Br]•– b (**4•–**)	2079 w, 2068 vw, 2026 m, 2014 s, 1992 s, br, 1971 sh, 1948 w, 1909 m, 1892 m
Os$_3$(CO)$_{10}$(BPM)[b] (**3**)	2086 w, 2035 s, 2003 sh, 1995 s, 1977 s, 1961 m, 1902 w
[Os$_3$(CO)$_{10}$(BPM)]•– b (**3•–**)	2075 w, 2063 w, 2017 s, 1989 sh, 1979 s, 1966 s, 1944 m, 1884 w
[Os$_3$(CO)$_{10}$(BPM)]•– b (**3′•–**)	2061 w, 1980 s, 1966 sh, 1892 m, 1872 m

[a] Measured at 213 K. [b] Measured at 293 K. [c] Measured in butyronitrile.
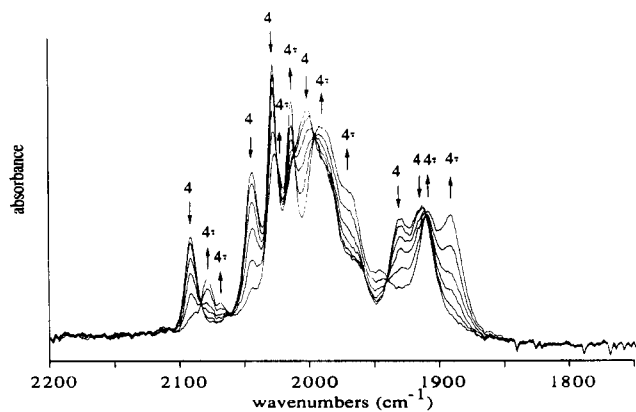

Figure 1. IR spectral changes in the ν(CO) region upon 1e$^-$ reduction of complex **4** ($\sim$10^{-2} M) in butyronitrile + 0.3 M Bu$_4$NPF$_6$ at the Pt-minigrid electrode at 293 K.

Complex **1** behaved differently since the reduction process was irreversible at room temperature. However, the follow-up chemical reaction of the reduction product could be slowed down and the metal–metal-bonded radical anion **1•–** could be detected and characterized by IR by performing the electrochemical reduction at 213 K in butyronitrile solution. Just as for **2** and **4** retention of the structure upon reduction of **1** to give **1•–** was

reflected in the close similarity of the ν(CO) IR pattern of these complexes with a shift to lower frequency. Even at 213 K a slow decomposition of **1•–** occurred with formation of [Mn(CO)$_5$]$^-$ (ν(CO) bands at 1902, 1862 cm^{-1}) and [Re(CO)$_3$(BPM)(n-PrCN)]• (n-PrCN = butyronitrile), which was further reduced to [Re(CO)$_3$(BPM)(n-PrCN)]$^-$ (ν(CO) bands at 1987, 1873, 1864 cm^{-1}) at the applied potential.

The above results show that splitting of the metal–metal bond occurs upon reduction of complexes **1** and **3** and that there is an energy barrier for this reaction. This splitting will be caused by the large polarization of this bond by the reduced BPM ligand. The σ-donor properties and polarization effects of the reduced BPM will be much smaller when this ligand acts as a bridge. As a result the metal–metal bond remained intact in the reduction products of complexes **2** and **4**.

A similar influence of the σ-donor properties of the reduced α-diimine ligand on the stability of the reduction products has recently been observed for the related complexes Re(Br)(CO)$_3$-(α-diimine).[18] Thus, reduction of Re(Br)(CO)$_3$(bpy) gave rise to release of Br$^-$ and formation of Re$_2$(CO)$_6$(bpy)$_2$, whereas reduction of Re(Br)(CO)$_3$(abpy) (abpy = azo-2,2′-bipyridine) produced stable [Re(Br)(CO)$_3$(abpy)]•– in which the Re–Br bond remained intact.

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