Electrochemical and IR/UV—Vis Spectroelectrochemical Studies of fac-[Mn(X)(CO)3(iPr-DAB)]n (n = 0, X = Br, Me, Bz; n = +1, X = THF, MeCN, nPrCN, P(OMe)3; iPr-DAB = 1,4-Diisopropyl-1,4-diaza-1,3-butadiene) at Variable Temperatures: Relation between Electrochemical and Photochemical Generation of [Mn(CO)3(α-diimine)]

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The title complexes [Mn(X)(CO)3(iPr-DAB)]n (n = 0, X = Br; n = +1, X = donor solvent) undergo a two-electron reduction according to an ECE sequence. The chemical step (C) involves prompt dissociation of the X ligand from the primary one-electron reduction product, followed by instantaneous one-electron reduction of the five-coordinate transient [Mn(CO)3(iPr-DAB)]n+ producing the anion [Mn(CO)3(iPr-DAB)]n−. The latter complex remains rather stable at T < 190 K, whereas at higher temperatures it undergoes an electron-transfer reaction with the parent complexes producing the dimer [Mn(CO)3(iPr-DAB)]2 (the second C step in the overall ECEC sequence). The rate of this reaction decreases in the order THF > MeCN > Br. The driving force for this behavior is the more positive E1/2 value of the redox couple [Mn(CO)3(iPr-DAB)]n+/n− relative to those of [Mn(X)(CO)3(iPr-DAB)]n+/n− and [Mn-(X)(CO)3(iPr-DAB)]n+/n− (X = donor solvent) and a very short lifetime of the primary reduction products. In contrast, the ligand P(OMe)3 in [Mn(P(OMe)3)(CO)3(iPr-DAB)]n+ is bound rather firmly at low temperatures, where the ECE sequence to [Mn(CO)3(iPr-DAB)]n− via [Mn(CO)3(iPr-DAB)]n− is only a minor route. The reduction of [Mn(X)(CO)3(iPr-DAB)] (X = Me, Bz) at room temperature affords the five-coordinate anion [Mn(CO)3(iPr-DAB)]− via dissociation of X from the one-electron-reduced intermediate [Mn(X)(CO)3(iPr-DAB)]n− detectable by cyclic voltammetry for X = Me. Oxidation of the five-coordinate anion [Mn(CO)3(iPr-DAB)]− produces the dimer [Mn(CO)3(iPr-DAB)]2, following the reverse ECE(C) sequence involved in the reduction path. The direct dimerization of the radicals primarily formed, [Mn(CO)3(iPr-DAB)]+, is probably only a minor alternative route. In the presence of excess P(OMe)3, the principal oxidation product is the cation [Mn(P(OMe)3)(CO)3(iPr-DAB)]+. The five-coordinate anions [Mn(CO)3(α-diimine)]− can be regarded as strongly π-delocalized complexes with the negative charge equally distributed over the α-diimine and CO ligands. The intriguing mechanism of their photochemical formation from fac-[Mn(X)(CO)3(α-diimine)] at low temperatures has been rectified on the basis of this (spectro)electrochemical study.

Introduction

Carbonyl complexes of the type [Re(X)(CO)3(α-diimine)]n+ (X = CO, halide, alkyl, organic donor) have been the subject of many photochemical,1 photophysical,2 and electrochemical3 studies, mainly due to their capability of mediating inter- and intramolecular electron-transfer reactions. Even though there are quite a few reports on the photochemistry of the Mn derivatives [Mn(X)(CO)3(α-diimine)] (X = halide,4–6 alkyl,7 metal fragment8–12), electrochemical studies of these com-
plexes are scarce. Recently, we presented a spectroelectrochemical study \(^{13}\) of \([\text{Mn}](\text{Cl})(\text{CO})_3(\text{bpy})]\) with the major goal of explaining the mechanism of the formation of the five-coordinate anion \([\text{Mn}](\text{CO})_3(\text{bpy})]\) on irradiation of \(\text{fac-}[\text{Mn}(\text{Br})(\text{CO})_3(\alpha-\text{dimine})]\) in 2-MeTHF at 153 K. \(^4\) In situ IR/UV–vis spectroelectrochemical experiments at room temperature revealed that the reduction of \([\text{Mn}](\text{Cl})(\text{CO})_3(\text{bpy})]\) produced, exclusively, the dimer \([\text{Mn}(\text{CO})_3(\text{bpy})]_2\), which converted in the subsequent cathodic step to the stable anion \([\text{Mn}](\text{CO})_3(\text{bpy})]^{-}\). At 223 K, however, \([\text{Mn}(\text{CO})_3(\text{bpy})]_2\) was produced simultaneously with \([\text{Mn}(\text{CO})_3(\text{bpy})]_2\). This observation was tentatively attributed to inhibited dimerization of the five-coordinate radicals \([\text{Mn}(\text{CO})_3(\text{bpy})]^{-}\) at temperatures below 220 K, \(^{11c}\) which allowed their direct reduction to \([\text{Mn}](\text{CO})_3(\text{bpy})]\). We have recently found, however, that the dimer \([\text{Mn}(\text{CO})_3(\text{bpy})]_2\) may also result from a coupling reaction between equivalent amounts of \([\text{Mn}(\text{CO})_3(\text{bpy})]^{-}\) and parent \([\text{Mn}](\text{CO})_3(\text{bpy})]\). This result points to an alternative route to \([\text{Mn}](\text{CO})_3(\text{bpy})]_2\) via an ECEC sequence described by eqs 1–4. In this sequence, the dimerization of reducible \([\text{Mn}](\text{Cl})(\text{CO})_3(\text{bpy})]^{-} + e^{-} \rightarrow [\text{Mn}](\text{Cl})(\text{CO})_3(\text{bpy})]^{2-}\) (1)

\([\text{Mn}](\text{Cl})(\text{CO})_3(\text{bpy})]^{2-} \rightarrow [\text{Mn}](\text{CO})_3(\text{bpy})]^{+} + \text{Cl}^{-}\) (2)

\([\text{Mn}](\text{CO})_3(\text{bpy})]^{+} + e^{-} \rightarrow [\text{Mn}](\text{CO})_3(\text{bpy})]^{-}\) (3)

\([\text{Mn}](\text{Cl})(\text{CO})_3(\text{bpy})]^{-} + [\text{Mn}](\text{CO})_3(\text{bpy})]^{-} \rightarrow [\text{Mn}](\text{CO})_3(\text{bpy})]_2 + \text{Cl}^{-}\) (4)

\([\text{Mn}](\text{CO})_3(\text{bpy})]^{-}\) cannot compete \(^{16}\) with the electrochemical reduction described by eq 3, as erroneously anticipated. \(^{13}\)

In this work, we describe the electrochemical reduction of the corresponding complexes fac-\([\text{Mn}](\text{X})(\text{CO})_3(\text{iPr-DAB})](\text{iPr-DAB})]\) \(^n\) \((n = 0, X = \text{Of}t, \text{Br}, \text{Me}, \text{Bz}; n = +1, \text{THF}, \text{MeCN}, \text{nPrCN})].\) Perusal of these results allows us to rectify the inaccurate \(^{13}\) mechanisms of the electrochemical and photochemical formation of the five-coordinate anions \([\text{Mn}](\text{CO})_3(\alpha-\text{dimine})]^{-}.\) Our interest in the electrochemical reduction of the complexes \([\text{Mn}](\text{X})(\text{CO})_3(\text{iPr-DAB})](\text{iPr-DAB})]\) \((X = \text{Me, Bz})\) relates to the one-electron reduction of the Re derivatives, which produces remarkably stable radicals \(\{[\text{Re}](\text{CO})_3(\text{iPr-DAB})]\) \(\rightarrow X^{-}\) \((X = \text{Me, Et, Bz})\). \(^{17}\)

The structure of the title complexes fac-\([\text{Mn}](\text{X})(\text{CO})_3(\text{iPr-DAB})](\text{iPr-DAB})]\) is schematically depicted in Figure 1.

**Experimental Section**

**Chemicals.** The solvents nPrCN (Fluka), MeCN (Acros Chimica), and THF (Acros Chimica) \(^{15}\) were dried on CaH\(_2\) (nPrCN and MeCN) or Na wire (THF) and distilled under nitrogen prior to use. The supporting electrolytes Bu\(_4\)NPF\(_6\) (Fluka) and Bu\(_4\)NB\(_2\)F\(_4\) (prepared from Bu\(_4\)NHSO\(_4\) and NaBF\(_4\)) were dried overnight under vacuum at 353 K and stored under argon before use. PPh\(_3\) (Aldrich) was recrystallized from a diethyl ether solution at 223 K. P(OMe)\(_3\) (Aldrich) was distilled from CaH\(_2\) under nitrogen before use. Ferrocene (BDH) and Ag(Otf\(_2\)) (Aldrich) \(^{15}\) were used as received.

The complexes \([\text{Mn}](\text{X})(\text{CO})_3(\text{iPr-DAB})](\text{iPr-DAB})]\) \((X = \text{Br, Otf, Me, Bz})\) were synthesized according to literature procedures and purified by column chromatography over Silica 60 (Merck), activated by heating overnight under vacuum at 433 K, with a gradient elution of n-hexane/THF. The purity of the complexes was checked by mass, UV–vis, IR, and \(^{1}H\) NMR spectroscopies.

The spectroelectrochemical samples were carefully prepared under an atmosphere of high-purity nitrogen or argon, using Schlenk techniques. The solutions of the light-sensitive complexes \([\text{Mn}](\text{X})(\text{CO})_3(\text{iPr-DAB})](\text{iPr-DAB})]\) \((X = \text{Me, Bz})\) were handled in the dark. The complexes \([\text{Mn}](\text{X})(\text{CO})_3(\text{iPr-DAB})](\text{iPr-DAB})]\) \((X = \text{Oft, Br})\) are less photoactive than the alkyl complexes, but still demanding the use of light-protected cells.

**Spectroelectrochemical Measurements and Instrumentation.** IR spectra were recorded on a Bio-Rad FTIR spectrometer (16 scans, resolution of 2 cm\(^{-1}\)). Electronic absorption spectra were measured on a Perkin-Elmer Lambda 5 UV–vis spectrophotometer, attached to a 3600 data station. IR and UV–vis spectroelectrochemical measurements at room temperature were performed in an OTTLE cell, \(^{19}\) equipped with a Pt microgrid working electrode (32 wires/cm) and CaF\(_2\) optical windows. For IR and UV–vis spectroelectrochemistry at low temperatures, we employed a purpose-made OTTLE cell \(^{20}\) which fitted into a liquid-nitrogen cryostat. \(^{21}\) A PA4 potentiostat (EKOM, Czech Republic) was used to carry out the controlled-potential electrolyses. The solutions were typi-
cally 3 × 10⁻¹ M in supporting electrolyte and 5 × 10⁻³ to 10⁻² M in the Mn complexes.

**Cyclic Voltammetry and Chronoamperometry.** Conventional cyclic voltammograms were recorded at 293 and 223 K in a light-protected CV cell equipped with a Pt disk working electrode of 500 μm diameter (polished carefully with a 0.25 μm diamond paste between scans), Pt gauze or coiled Pt wire auxiliary electrodes, and SCE (Taucussel) or a coiled Ag wire normal reference and pseudoreference electrodes, respectively. (Notably, all of the Mn complexes under study strongly adsorb at Au disk electrodes.) The redox potentials are reported against the standard Fc/Fc⁺ reference electrode was a Pt wire. At the end of the experiment, the reference electrode was a Pt wire. At the end of the experiment, ferrocene was added to the solution for calibration. The auxiliary electrode was a Pt spiral of ca. 1 cm² surface area. It was placed within a 1 cm distance from the working electrode, facing it. The same potentialist23 was used. The signal generator and digital oscilloscope were, in this case, a HP-3314A and a two-channel HP-54510A (8 bits; 1 ns dwell time; 250 MHz), respectively.

**Table 1.** IR ν(CO) and UV–Vis Data for fac-[Mn(X)(CO)₃(iPr-DAB)]⁺ (n = 0, X = Br, OtF, Me, Bz; n = +1, X = nPrCN, P(OMe)₃) and Their Reduction Products (in nPrCN, unless Stated Otherwise)

<table>
<thead>
<tr>
<th>complex</th>
<th>T [K]</th>
<th>ν(CO) [cm⁻¹]</th>
<th>kₛᵥ [Nm⁻¹]</th>
<th>λₘₐₓ (λₘₐₓ) [nm]</th>
<th>[cm⁻¹ M⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(OTf)(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>2041 (s), 1939 (s, f)</td>
<td>1573</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mn(Br)(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>2040 (s), 1954 (s), 1934 (s)</td>
<td>1578</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mn(Me)(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>2024 (s), 1934 (m), 1924 (m)</td>
<td>1553</td>
<td>477 (2650)</td>
<td></td>
</tr>
<tr>
<td>[Mn(Bz)(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>1998 (s), 1897 (s)</td>
<td>1501</td>
<td>495 (4600), 343</td>
<td></td>
</tr>
<tr>
<td>[Mn(nPrCN)(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>2046 (s), 1955 (s, br)</td>
<td>1505</td>
<td>502 (5100)</td>
<td></td>
</tr>
<tr>
<td>[Mn(OtF)(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>1986 (s), 1916 (m), 1961 (m)</td>
<td>1591</td>
<td>405 (3000)</td>
<td></td>
</tr>
<tr>
<td>[Mn(P(OMe)₃)(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>2047 (s), 1977 (s, br), 1941 (s)</td>
<td>1598</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mn(P(OMe)₃)(CO)₃(iPr-DAB)]⁺</td>
<td>193</td>
<td>1969 (s), 1899 (s)</td>
<td>1511</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mn(P(OMe)₃)(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>2023 (s), ~1925 (br)</td>
<td>1554</td>
<td></td>
<td></td>
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<tr>
<td>[Mn(THF)(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>2017 (s), 1932 (s), 1894 (s)</td>
<td>1533</td>
<td>460 (2000), 380,360,300</td>
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<tr>
<td>[Mn(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>2004 (s), 1914 (vs), 1894 (vs)</td>
<td>1517</td>
<td></td>
<td></td>
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<tr>
<td>[Mn(OTf)(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>1975 (w), 1945 (s), 1886 (m, br)</td>
<td>1536</td>
<td>744 (9650), 550, 480, 370</td>
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<tr>
<td>[Mn(THF)(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>1977 (w), 1959 (sh, sw), 1948 (s)</td>
<td>1537</td>
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<td></td>
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<tr>
<td>[Mn(OTf)(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>1896 (w), 1887 (m)</td>
<td>1538</td>
<td></td>
<td></td>
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<tr>
<td>[Mn(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>1919 (s), 1811 (s, br)</td>
<td>1379</td>
<td>490 (3300), 365 (650)</td>
<td></td>
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<tr>
<td>[Mn(OtF)(CO)₃(iPr-DAB)]⁺</td>
<td>293</td>
<td>1919 (s), 1822 (s), 1778 (s)</td>
<td>1368</td>
<td>485, 386</td>
<td></td>
</tr>
<tr>
<td>[Mn(THF)(CO)₃(iPr-DAB)]⁺</td>
<td>193</td>
<td>1923 (s), 1815 (s, br)</td>
<td>1385</td>
<td>438, 386</td>
<td></td>
</tr>
</tbody>
</table>

a In THF, b In the presence of Bu₄NPF₆. c An unidentified side product. d ν(CO) bands of the corresponding radical [Mn(P(OMe)₃)(CO)₃(iPr-PyCa)]⁺ (iPr-PyCa is defined in ref 15) found at 2024 (s), 1942 (s) and 1909 (cm⁻¹ (135 K, 2-MeTHF)). e Reference 7, f As the Na⁺ salt.

Table 2. Redox Potentials (V vs E_{1/2} (Fc/Fc')) of fac-(Mn(X)(CO)_3(iPr-DAB)) (n = 0, X = Br, Me, Bz; n = +1, X = nPrCN, MeCN, THF, P(OMe)_3, PPh_3) and Their Reduction Products^a

<table>
<thead>
<tr>
<th>complex</th>
<th>E_{pa}</th>
<th>E_{pc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(OMe)(CO)_3(iPr-DAB)]^-</td>
<td>-0.88</td>
<td>-0.86</td>
</tr>
<tr>
<td>[Mn(THF)(CO)_3(iPr-DAB)]^-</td>
<td>-1.78</td>
<td>-1.66</td>
</tr>
<tr>
<td>[Mn(MeCN)(CO)_3(iPr-DAB)]^-</td>
<td>-0.88</td>
<td>-0.86</td>
</tr>
<tr>
<td>[Mn(MeCN)(CO)_3(iPr-DAB)]^0</td>
<td>0.08</td>
<td>0.24</td>
</tr>
<tr>
<td>[Mn(PPH_3)(CO)_3(iPr-DAB)]^-</td>
<td>-0.88</td>
<td>-0.86</td>
</tr>
<tr>
<td>[Mn(P(OMe)_3)(CO)_3(iPr-DAB)]^-</td>
<td>-1.78</td>
<td>-1.66</td>
</tr>
<tr>
<td>[Mn(P(OMe)_3)(CO)_3(iPr-DAB)]^+</td>
<td>0.08</td>
<td>0.24</td>
</tr>
<tr>
<td>[Mn(CO)(iPr-DAB)]^-</td>
<td>-0.88</td>
<td>-0.86</td>
</tr>
<tr>
<td>[Mn(CO)(iPr-DAB)]^-</td>
<td>-0.88</td>
<td>-0.86</td>
</tr>
</tbody>
</table>

^a The redox potentials of corresponding bpy-complexes are included for comparison. Conditions and definitions: Cyclic voltammetry; 2 × 10^{-3} M solutions in THF containing 3 × 10^{-1} M Bu_4NPF_6, v = 100 mV/s, Pt disk working electrode. E_{1/2} (Fc/Fc') = +0.575 V vs SCE. ^b Same conditions as in MeCN. E_{1/2} (Fc/Fc') = +0.425 V vs SCE. ^c Same conditions as b except in nPrCN. ^d Reduction of the complex; E_{pa} = anodic peak potential. 

Results

IR and UV–Vis Spectroelectrochemistry. In the following sections, the spectroscope changes accompanying the redox step to reduce the Mn complexes. Reliable I_L/M values were indicated by a negligible difference between the initial and final I_L/F currents. This procedure led to the following values of R_Li = \((I_{L_{av}}/I_{F_{av}})_{(G_{av}/G_{av})} = n_{app} D_{Mn}/D_{iPrDAB} = 1.05; R_{Lli} = 1.06; R_{Lsi} = 0.41; R_{Lri} = 0.98.

Extraction of the n_{app} and D values from the combined expressions for R_{chrono} and R_{lim} gave (a) for the reduction of [Mn(OMe)(CO)_3(iPr-DAB)] in THF (S_a) n_{app} = 1.92 ± 0.08 and D_{Mn} = (0.55 ± 0.02)D_{Fc} (b) for the reduction of [Mn(OMe)(CO)_3(iPr-DAB)] in MeCN (S_b) n_{app} = 1.96 ± 0.08 and D_{Mn} = (0.55 ± 0.02)D_{Fc} (c) for the reduction of [Mn(OMe)(CO)_3(iPr-DAB)] in THF (S_c) n_{app} = 0.85 ± 0.15 and D_{Mn} = (0.48 ± 0.07)D_{Fc} (d) for the reduction of [Mn(CO)(iPr-DAB)] in MeCN (S_d) n_{app} = 1.86 ± 0.10 and D_{Mn} = (0.55 ± 0.06)D_{Fc}.

Using the known D_{Fc} values in THF (8.0 × 10^{-6} cm^2 s^{-1}) and MeCN (1.5 × 10^{-5} cm^2 s^{-1})\(^{19}\) gives, for example, D_{Mn} [Mn(OMe)(CO)_3(iPr-DAB)] = 4.4 × 10^{-3} (in THF) and 1.03 × 10^{-3} (in MeCN) cm^2 s^{-1}. The characteristic time for the steadystate measurement\(^{22}\) is then T = r_{p}D/D = 227 (in THF) or 97 ms (in MeCN), which indeed falls within the range T = \(\theta\) = 50–300 ms chosen for the chronoamperometric measurements with the 500-μm Pt disk, thus validating the determined values of n_{app} and D_{Mn}. The value \(\theta\) = 227 ms corresponds to the CV scan rate \(v\) = 110 mV/s. This result implies that the reduction of [Mn(OMe)(CO)_3(iPr-DAB)] in THF at the voltammetric scan rate \(v\) = 100 mV/s corresponds to a two-electron process (see eqs 1–3).

(25) The average C=O force constants k_w of these species in Table 1 were calculated using eq 5. Exact determination of all four CO force constants, \(k_{OMe}\), \(k_{CN}\), \(k_{MeCN}\), \(k_{THF}\), by the Cotton–Kraihanzel energy factorized field methods\(^{23,28}\) was not possible due to the lack of the wavenumbers of the CO-enriched positional isomers. The empirical method of Timney\(^{29}\) was also not applied as the exact geometry of the five-coordinate reduced complexes was unknown. Equation 5: \(k_{OMe} = 4.0383 \times 10^{-4} \left(\Sigma_{g}\nu_{w}\right)/\Sigma g\), where \(g\) = degeneracy of the ith CO stretching mode of the frequency \(\nu_{w}\) (in cm^{-1}).


the dimer \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\) gave rise to two strong \((\text{see Figure 2a and Table 1})\). Subsequent reduction of \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\) at a more positive potential \((\text{see Table 2})\).

The initial reduction step producing the dimer \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\) \(10,11\) like \([\text{Mn(CO)}_3(\text{bpy})]_2\) \(12,13\) and \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\) \(10,11\) also.

The formation of the stable metal-bonded dimer \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\) \(10,11\) and \([\text{Re}-(\text{X})(\text{CO})_3(\text{iPr-DAB})]_2\) \(20,30,31\) and \([\text{Ru}-(\text{X})(\text{CO})_3(\text{iPr-DAB})]_2\) \(30\) \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\) also possesses an eclipsed conformation \((C_2v\text{ point group})\) in solution. Apart from this dimer, \(\nu(\text{CO})\) bands of a minor unassigned species \(P_1\) were detected in the IR spectrum \((\text{see Figure 2a and Table 1})\). Subsequent reduction of the dimer \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\) gave rise to two strong \(\nu(\text{CO})\) bands at 1919 and 1811 \((\text{br})\) cm\(^{-1}\) \((\text{Figure 2b})\) which belong to the stable five-coordinate anion \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\). This assignment is in line with the similar \(\nu(\text{CO})\) wavenumbers of \([\text{Mn(CO)}_3(\text{bpy})]^{-4,13}\) Related anions are typically formed on two-electron reduction of \([\text{Ru}(\text{X})(\text{R})(\text{CO})_2(\alpha\text{-dimine})]^{20,30,31}\) and \([\text{Re}(\text{X})(\text{CO})_3(\alpha\text{-dimine})]^{3a,3b,17}\) \((X=\text{halide}, R=\text{alkyl})\) containing basic \(\alpha\text{-dimine} \text{ligands} \). The origin of the visible absorption of \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\) \((\text{see Figure 3b and Table 1})\) is discussed below. Reoxidation of \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\) in nPrCN at 293 K only yielded the dimer \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\). \([\text{Mn(nPrCN)(CO)}_3(\text{iPr-DAB})]^-\) was ultimately recovered on the subsequent oxidation of the dimer at a more positive potential \((\text{see Table 2})\).

The OTTLE experiment with \([\text{Mn(nPrCN)(CO)}_3(\text{iPr-DAB})]^-\) \(198\) K was also carried out at 198 K in nPrCN. The reduction directly yielded the two-electron-reduced anion \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\). The dimer \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\) was only produced at a very low concentration \((\text{see Figure 4, Supporting Information})\). No additional \(\nu(\text{CO})\) bands were observed, which might indicate formation of 18-electron radicals \([\text{Mn(nPrCN)(CO)}_3(\text{iPr-DAB})]^-\).

The cation \([\text{Mn(nPrCN)(CO)}_3(\text{iPr-DAB})]^-\) \(30\) was also reduced at room temperature in the presence of a 200-fold excess of PhCHO. The large excess of PhCHO had, however, no effect on the quantitative yield of the dimer \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\). This result demonstrates that PhCHO, similarly to nPrCN, does not stabilize the transient radical \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\) \((\text{see below})\) in the course of the cathodic process.

In the presence of 1 equiv of PhCO, \([\text{Mn(nPrCN)(CO)}_3(\text{iPr-DAB})]^-\) \(30\) first converted via an electrode-catalyzed reaction \(3a\) into \([\text{Mn(PhCO)}_3(\text{iPr-DAB})]^-\) \(30\) \((\text{see Table 1})\). In the presence of a 200-fold excess of PhCO, \([\text{Mn(PhCO)}_3(\text{iPr-DAB})]^-\) was only observed as a transient species. The electrode-catalyzed reaction then ultimately gave the dicarbonyl derivative \([\text{Mn(PhCO)}_3(\text{iPr-DAB})]^-\) \(30\) \((\text{see Table 1})\). Subsequent reduction of the latter cation was accompanied by secondary chemical and electron-transfer reactions that mainly produced the anion \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\) \(30\) and was not further investigated. The cations \([\text{Mn(PhCO)}_3(\text{iPr-DAB})]^-\) \(30\) remained stable at 183–198 K. Their reduction then yielded the 18e radicals \([\text{Mn(PhCO)}_3(\text{iPr-DAB})]^-\) \(30\) \((\text{see Table 1})\), concomitantly with a small amount of \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\). This result indicates that \([\text{Mn(PhCO)}_3(\text{iPr-DAB})]^-\) slowly lose PhCO to give the five-coordinate radicals \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\) \(30\) \((\text{see Table 1})\). This assumption was corroborated by the cyclic voltammetric results \((\text{see below})\). Subsequent reduction of \([\text{Mn(PhCO)}_3(\text{iPr-DAB})]^-\) \(30\) led to complete dissociation of the PhCO ligand, producing \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\) \(30\). Notably, reoxidation of the five-coordinate anion in the presence of PhCO led directly to the recovery of the parent cation \([\text{Mn(PhCO)}_3(\text{iPr-DAB})]^-\) \(30\).

\([\text{Mn(Ph)(CO)}_3(\text{iPr-DAB})]^-\). According to the IR and UV–vis OTTLE results, reduction of \([\text{Mn(Ph)(CO)}_3(\text{iPr-DAB})]^-\) \(198\) K at room temperature simultaneously afforded both the dimer \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\) and the anion \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\). Reoxidation of the ultimate reduction product \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\) \(198\) K simultaneously produced both \([\text{Mn(Ph)(CO)}_3(\text{iPr-DAB})]^-\) and the dimer \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\). This observation implies that the conversion of \([\text{Mn(Ph)(CO)}_3(\text{iPr-DAB})]^-\) \(198\) K to the reduction and vice versa on the reoxidation does not pass via the intermediate \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\) \(198\) K. Unambiguous evidence for this mechanistic assumption was gained from the cyclic voltammetric studies \((\text{see below})\).

Finally, the starting complex \([\text{Mn(Ph)(CO)}_3(\text{iPr-DAB})]^-\) \((X=\text{Me, Bz})\) was completely recovered on subsequent oxidation of \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\) at more positive potentials \((\text{see Table 2})\) due to the rapid recoordination of Br in the thin solution layer.

\([\text{Mn(X)(CO)}_3(\text{iPr-DAB})]^-\) \((X=\text{Me, Bz})\). Reduction of \([\text{Mn(X)(CO)}_3(\text{iPr-DAB})]^-\) \((X=\text{Me, Bz})\) at room temperature, monitored by IR and UV–vis spectroscopies,
directly afforded the anion \([\text{Mn(CO)}_3(\text{iPr-DAB})^-]\) (see Table 1). Reoxidation of the anion produced, in this case, a carbonyl species with strong \(\nu(\text{CO})\) bands at 2023, 1934, and 1919 cm\(^{-1}\) (for \(X = \text{Bz}\)) and at 2023 and 1923 (br) cm\(^{-1}\) (for \(X = \text{Me}\)). These wavenumbers closely resemble those of the as yet unidentified product P\(_1\), as well as those of neutral \([\text{Mn(Br)(CO)}_3(\text{iPr-DAB})]\) (see Table 1). Formation of the dimer \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\) was not observed. Reduction of \([\text{Mn(Bz)(CO)}_3(\text{iPr-DAB})]^-\) at 198 K yielded two products in nearly equal concentration, viz. the anion \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\) and a tricarbonyl complex with \(\nu(\text{CO})\) bands at 1985, 1882, and 1873 cm\(^{-1}\). The latter product was thermally unstable. The reduction of \([\text{Mn(Me)(CO)}_3(\text{iPr-DAB})]^-\) at 198 K yielded \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\) only as a minor product. Further experiments need to be performed in this area.

**Cyclic Voltammetry.** \([\text{Mn(X)}_n(\text{iPr-DAB})]_n^0\) (n = 0, \(X = \text{Br}\); n = +1, \(X = \text{MeCN}, \text{THF}\)). The cyclic voltammograms of the complexes \([\text{Mn(Br)}_n(\text{CO})_3(\text{iPr-DAB})]_n^0\), in MeCN and THF, \([\text{Mn(MeCN)}_n(\text{CO})_3(\text{iPr-DAB})]_n^+\), and \([\text{Mn(THF)}_n(\text{CO})_3(\text{iPr-DAB})]_n^+\) are depicted in Figures 5A, B, 6 (Supporting Information), 7A, B (7B in Supporting Information), and 8, respectively.

**Reduction Paths.** The cyclic voltammogram of the complex \([\text{Mn(Br)}(\text{CO})_3(\text{iPr-DAB})]_2\) in MeCN at \(n = 100\) mV/s shows a single cathodic peak at \(E_{\text{pc}} = -1.57\) V (Figure 5A), which corresponds to the total transfer of two electrons (\(n_{\text{app}} = 1.95\)). The predominant \(\pi^*\)(iPr-DAB) character of the LUMO of \([\text{Mn(Br)}(\text{CO})_3(\text{iPr-DAB})]_2^+\) implies that the reduction initially affords the radical anion \([\text{Mn(Br)}(\text{CO})_3(\text{iPr-DAB})]^-\), which rapidly loses the Br– ligand and converts to the coordinatively unsaturated radical \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2^+\). This transient species is then instantaneously reduced with the second electron, resulting in the formation of the five-coordinate anion \([\text{Mn(CO)}_3(\text{iPr-DAB})]_-\). Importantly, we have independently proved that the two-electron-reduced anion \([\text{Mn(CO)}_3(\text{iPr-DAB})]_-\) reacts smoothly with an equivalent amount of \([\text{Mn(Br)}(\text{CO})_3(\text{iPr-DAB})]_2\) to give the dimer \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\) as the single product. There was, however, no evidence to suggest the presence of the dimer \([\text{Mn(CO)}_3(\text{iPr-DAB})]_2\) on the time scale defined by scan rates \(v \geq 50\) mV/s. Simultaneous formation of \([\text{Mn(CO)}_3(\text{iPr-DAB})]_-\) and the dimer was nevertheless confirmed by the corresponding spectroelectrochemical experiments on the seconds time scale (see above). \([\text{Mn(CO)}_3(\text{iPr-DAB})]^-\) is thus formed via the ECE sequence as described by eqs 1–3 and summarized in Scheme 1. An alternative route to this anion might be the DISP 1 sequence defined by eqs 6 and 7. Revealing evidence against the disproportionation route of \([\text{Mn(Br)}(\text{CO})_3(\text{iPr-DAB})]_2\) is the crossed voltammetric response in Figures 5A and 6. This characteristic feature is in fact equivalent to a hump on the corresponding chronoamperometric anodic current trace, crossing the line of zero current, which is claimed for the ECE sequence but never for the DISP 1 path.\(^{32}\) We assume that the ECE mechanism is favored.

by very fast dissociation of the Br\textsuperscript{-} ligand from the radical anion [Mn(Br)(CO)\textsubscript{3}(iPr-DAB)]\textsuperscript{2-} (see eq 2) prior to its diffusion into the bulk solution, which permits further reduction of the transient radical [Mn(CO)\textsubscript{3}(iPr-DAB)]\textsuperscript{•} still at the electrode surface. Reoxidation of

[Mn(Br)(CO)\textsubscript{3}(iPr-DAB)]\textsuperscript{•-} +

[Mn(CO)\textsubscript{3}(iPr-DAB)]\textsuperscript{•} → [Mn(Br)(CO)\textsubscript{3}(iPr-DAB)] +

[Mn(CO)\textsubscript{3}(iPr-DAB)]\textsuperscript{+} (6)

[Mn(X)(CO)\textsubscript{3}(iPr-DAB)]\textsuperscript{•} + [Mn(CO)\textsubscript{3}(iPr-DAB)]\textsuperscript{•} →

[Mn(X)(CO)\textsubscript{3}(iPr-DAB)]\textsuperscript{•} + [Mn(CO)\textsubscript{3}(iPr-DAB)]\textsuperscript{•+} (7)

[Mn(Br)(CO)\textsubscript{3}(iPr-DAB)]\textsuperscript{•-} could not, indeed, be observed even at v = 4 × 10\textsuperscript{5} V/s, which allows an estimation\textsuperscript{33} of the lower limit of the cleavage rate constant of [Mn(Br)(CO)\textsubscript{3}(iPr-DAB)]\textsuperscript{•-}: k \gg 10\textsuperscript{7} s\textsuperscript{-1}. The upper limit is obviously k < KT/h (∼10\textsuperscript{12} s\textsuperscript{-1}).

For the reduction of [Mn(Br)(CO)\textsubscript{3}(iPr-DAB)] in MeCN, the scan rate dependence of the cathodic-peak potential, δE\textsubscript{p,c}/δ(log(v)), is a straight line with a slope of -30 mV decade\textsuperscript{-1} within the interval v = 0.1–2.0 V/s (see Figure 9a). This value characterizes a monomolecular E\textsubscript{Ci} mechanism\textsuperscript{35} represented herein by eqs 1 and 2, implying that the dissociation of Br\textsuperscript{-} from [Mn(Br)(CO)\textsubscript{3}(iPr-DAB)]\textsuperscript{•-} is the rate-determining step in the ECE reduction path of [Mn(Br)(CO)\textsubscript{3}(iPr-DAB)] in Scheme 1. The electron transfer becomes irreversible for v > 2 V/s, which corresponds to the observed slope of -60 mV decade\textsuperscript{-1} (see Figure 9a). The normalized cathodic

(33) For an E\textsubscript{Ci} mechanism, a cyclic voltammetric response to an electron transfer step remains chemically totally irreversible at a particular scan rate v provided\textsuperscript{34} the follow-up rate constant k \gg 10\textsuperscript{9} s\textsuperscript{-1}, where k = ΔE\textsubscript{p,c}/δ(log(v)) and ΔE\textsubscript{p,c} = E\textsubscript{p,c} + E\textsubscript{a,a} – 2E\textsubscript{c} (E\textsubscript{c} is the switching potential, ca. 300 mV behind the E\textsubscript{p,c} value). In our case, v = 4 × 10\textsuperscript{5} V/s, hence k \gg 10 (v/ΔE\textsubscript{p,c}) = 7 × 10\textsuperscript{8} s\textsuperscript{-1} (~10\textsuperscript{11} s\textsuperscript{-1}).


current 1.2 V remains fairly constant at the moderate scan rates where the ECI mechanism applies. This result is in line with the hindered coupling reaction between [Mn(CO)₃(iPr-DAB)]⁻ and [Mn(Br)(CO)₃(iPr-DAB)]⁻, corresponding to eq 4, on this time scale.

Considering the ECI(E) reduction path of [Mn(Br)-(CO)₃(iPr-DAB)], the known relationship 35 between the zero-electron coupling reaction between [Mn(CO)₃(iPr-DAB)]⁻ and the known relationship 35 between the zero-electron coupling reaction between [Mn(CO)₃(iPr-DAB)]⁻ and the anodic peak of [Mn(CO)₃(iPr-DAB)]⁻, rather small in MeCN on the timescale defined by the above k limits predicts that the E₁/₂ value of the redox couple [Mn(CO)₃(iPr-DAB)]⁻ lies in the interval −1.85 V < E₁/₂ < −1.71 V vs Fc/Fc⁺, i.e., much more negatively than E₁/₂ of the redox couple [Mn(CO)₂(iPr-DAB)]⁺ (see below). From this comparison, it is thus obvious that the five-coordinate radicals [Mn(CO)₃(iPr-DAB)]⁻ have to be reduced instantaneously to the corresponding anions at the reduction potential of parent [Mn(Br)(CO)₃(iPr-DAB)]. Their consecutive dimerization to [Mn(CO)₃(iPr-DAB)]₂ therefore, cannot compete with this cathodic step, as shown in Scheme 1; instead, the dimer is only formed via the coupling reaction following eq 4.

The same two-electron reduction path can be drawn for the reduction of the cations [Mn(X)(CO)₃(iPr-DAB)]⁺ (X = MeCN, THF), where the transient [Mn(CO)₃(iPr-DAB)]⁺ originates from the unstable radicals [Mn(X)(CO)₃(iPr-DAB)]⁺ (see Scheme 1). Notably, the cyclic voltammogram of [Mn(MeCN)(CO)₃(iPr-DAB)]⁺ at room temperature and v = 100 mV/s (Figure 7A) shows an additional, small cathodic peak at Eₚ,c = −1.64 V due to the reduction of [Mn(CO)₃(iPr-DAB)]⁻ in agreement with n_app = 1.86.36 This cathodic peak becomes diminished on increasing the scan rate (see Figure 7B), as the zero-electron coupling reaction between [Mn(CO)₃(iPr-DAB)]⁻ and parent [Mn(MeCN)(CO)₃(iPr-DAB)]⁺ is too slow to produce a detectable amount of [Mn(CO)₃(iPr-DAB)]₂ at v ≳ 2 V/s. On the OTTLE time scale of 10⁻¹–10² s, however, only [Mn(CO)₃(iPr-DAB)]₂ is produced in this case (see above).

On the other hand, the well-developed cathodic peak of [Mn(CO)₃(iPr-DAB)]⁻ at Eₚ,c = −1.73 V for v = 100 mV/s (see Figure 8) shows that [Mn(THF)(CO)₃(iPr-DAB)]⁺ reacts with the anion [Mn(CO)₃(iPr-DAB)]⁻ considerably more rapidly than the MeCN- and, in particular, Br-derivatives (see Scheme 1). The reduction of the cation at Eₚ,c = −1.19 V then corresponds to the total transfer of one electron, in agreement with experimentally determined n_app = 0.85 ± 0.15. The above coupling reaction becomes less competitive on increasing the scan rate to v = 2 V/s, where dE_p,a/dlog(v) = −30 mV decade⁻¹ still applies, which is reflected in the slightly increasing function d(log(v)/v⁻¹/₂)/dlog(v) due to n_app > 1, see Figure 9b.

Reoxidation Paths. Oxidation of [Mn(CO)₃(iPr-DAB)]⁻ (E_p,a in Table 2, see Figures 5–8) produces, at room temperature, the radicals [Mn(CO)₃(iPr-DAB)]. Cyclic voltammograms of parent [Mn(Br)(CO)₃(iPr-DAB)] (Figures 5A and 6) show that these radicals do not concomitantly dimerize, as the detectable amount of [Mn(CO)₃(iPr-DAB)]₂ oxidized at E_p,a = −0.24 V is rather small in MeCN on the time scale defined by v = 100 mV/s and only slightly larger in THF. Scan reversal beyond the anodic peak of [Mn(CO)₃(iPr-DAB)]⁺ in MeCN reveals a new cathodic peak at −1.26 V due to the reduction of [Mn(MeCN)(CO)₃(iPr-DAB)]⁺, whose peak current considerably increases at higher scan rates and on repeated scans (see Figure 5B).

The radicals [Mn(CO)₃(iPr-DAB)]⁺ preferably take up the solvent molecules and convert to [Mn(MeCN)(CO)₃(iPr-DAB)]⁺, which instantaneously oxidize at the applied oxidation potential of [Mn(CO)₃(iPr-DAB)]⁺ (see Table 2), to the corresponding cations detectable on the reverse cathodic scan (see Scheme 1). This E(C) sequence, where the rate-determining step is the pseudo-first-order chemical reaction of [Mn(CO)₃(iPr-DAB)]⁺ with the MeCN solvent, was unequivocally confirmed by the scan-rate dependence of the E_p,a potential of [Mn(CO)₃(iPr-DAB)]⁺: δE_p,a/log(v) = 30 mV decade⁻¹ for v = 0.05–2 V/s.35 For the consecutive dimerization of [Mn(CO)₃(iPr-DAB)]⁺ as a second-order reaction, δE_p,a/log(v) = 20 mV decade⁻¹ should be observed.35 The same situation applies for the oxidation of [Mn(CO)₃(iPr-DAB)]⁺ in THF which produces [Mn(THF)(CO)₃(iPr-DAB)]⁺. The detection of the latter cations on the reverse cathodic scan, however, demands considerably higher scan rates relative to the detection limit for [Mn(MeCN)(CO)₃(iPr-DAB)]⁺, viz. v = 500 V/s vs 0.1 V/s at room temperature, respectively. The spectroelectrochemical experiments have shown that the solvent ligand X in [Mn(X)(CO)₃(iPr-DAB)]⁺ becomes readily substituted by the Br- anions liberated on reduction of [Mn(Br)(CO)₃(iPr-DAB)]. This substitution reaction is faster for X = THF than that for X = MeCN. It leads to the recovery of parent [Mn(Br)(CO)₃(iPr-DAB)] whose subsequent zero-electron-coupling reaction with non-oxidized [Mn(CO)₃(iPr-DAB)]⁻ to give [Mn(CO)₃(iPr-DAB)]⁺ (see Scheme 1) is rather slow relative to that of [Mn(X)(CO)₃(iPr-DAB)]⁺ (X = THF, MeCN) and is hardly observable on the time scale of cyclic voltammetry defined by v ≥ 50 mV/s. This implies that the corresponding reaction rate constant must be less than a few hundred M⁻¹ s⁻¹.134 The higher stability of [Mn(CO)₃(iPr-DAB)]⁺ toward the nucleophilic attack of [Mn(CO)₃(iPr-DAB)]⁻ then explains the simultaneous IR OTTLE detection of [Mn(CO)₃(iPr-DAB)]₂ and [Mn(CO)₂(iPr-DAB)]⁺ during the oxidation of [Mn(CO)₂(iPr-DAB)]⁻ produced from [Mn(Br)(CO)₃(iPr-DAB)] at room temperature and on the other hand, the exclusive formation of [Mn(CO)₃(iPr-DAB)]⁺ in the absence of uncoordinated Br⁻ (see above).

[Mn(P(OMe)₃)₂(CO)₃(iPr-DAB)]⁺. The cyclic voltammogram of the cation [Mn(P(OMe)₃)₂(CO)₃(iPr-DAB)]⁺ in nPrCN at 223 K showed a chemically reversible cathodic process at E_p,c = −1.36 V due to the formation of [Mn(P(OMe)₃)₂(CO)(iPr-DAB)]⁻. This radical complex is not completely stable at room temperature. In the spectroelectrochemical section, we have documented that T ≈ 190 K was needed to stabilize [Mn(P(OMe)₃)₂(CO)(iPr-DAB)]⁻ on the time scale of minutes. The subsequent reduction of [Mn(P(OMe)₃)₂(CO)(iPr-DAB)]⁻ was found at E_p,c = −2.38 V. This cathodic step was chemically irreversible and produced [Mn(CO)₃(iPr-DAB)]⁺, as indicated by the appearance of its anodic peak.
peak at $E_{\text{pa}} = -1.20 \text{ V}$ (see Table 2) on the reverse scan. Addition of excess $\text{P(OMe)}_3$ into the solution of $[\text{Mn-(P(OMe)}_3\text{)(CO)}_3\text{)(iPr-DAB)}]^{\text{2-}}$ at room temperature resulted in a significant decrease of the peak at $E_{\text{pc}} = -1.36 \text{ V}$ in favor of a new cathodic peak at $E_{\text{pc}} = -1.66 \text{ V}$ attributed to the reduction of the dicarbonyl cation $[\text{Mn(P(OMe)}_3\text{)(CO)}_2\text{(iPr-DAB)}]^{\text{2+}}$. In line with the spectroelectrochemical experiments, this electrocatalytic reaction became completely inhibited at 223 K.

Importantly, there was no evidence for the formation of the dimer $[\text{Mn(CO)}_3\text{(iPr-DAB)}]_2$ ($E_{\text{pa}} = -0.24 \text{ V}$) on the reoxidation of $[\text{Mn(CO)}_3\text{(iPr-DAB)}]^{\text{2-}}$ in the presence of excess $\text{P(OMe)}_3$, which also agrees with the above OTTLE results.

On the basis of the combined spectroelectrochemical/cyclic voltammetric evidence, the redox cycle of $[\text{Mn-(P(OMe)}_3\text{)(CO)}_3\text{(iPr-DAB)}]^{\text{2-}}$ is summarized in Scheme 2.

$[\text{Mn(X)(CO)}_3\text{(iPr-DAB)}]^{\text{2-}}$ (X = Me, Bz). The complex $[\text{Mn(Bz)(CO)}_3\text{(iPr-DAB)}]$ is reduced slightly more positively than the derivative with the more electron-releasing Me group (see Table 2).\(^{(39)}\) Scan reversal beyond the cathodic peaks of $[\text{Mn(Me)(CO)}_3\text{(iPr-DAB)}]$ and $[\text{Mn(Bz)(CO)}_3\text{(iPr-DAB)}]$ showed an anodic peak at $E_{\text{pa}} = -1.22 \text{ V}$ belonging to the oxidation of $[\text{Mn(CO)}_3\text{(iPr-DAB)}]^{\text{2-}}$. Identical with $[\text{Mn(Br)(CO)}_3\text{(iPr-DAB)}]$, the Me derivative initially undergoes a one-electron reduction which gives the corresponding radical anion (eq 8).

$[\text{Mn(Me)(CO)}_3\text{(iPr-DAB)}]^{\text{2-}}$ is however, considerably more stable than $[\text{Mn(Br)(CO)}_3\text{(iPr-DAB)}]^{\text{2-}}$, as its reoxidation could still be observed on the reverse anodic scan (see Figure 10).

In contrast to the two-electron (ECE) reduction path of $[\text{Mn(Br)(CO)}_3\text{(iPr-DAB)}]$ (see Scheme 1), we assume that the secondary chemical reaction of the radical anion $[\text{Mn(Me)(CO)}_3\text{(iPr-DAB)}]^{-}$ directly produces anion $[\text{Mn(Me)(CO)}_3\text{(iPr-DAB)}]^{\text{-}}$ as the only carbonyl species detected during the corresponding IR OTTLE experiment at room temperature and the radical Me$^+$ whose fate was not studied (eq 9). Recall that the spectroscopic properties of the related stable radical anions $[\text{Re(X)(CO)}_3\text{(iPr-DAB)}]^{-}$ (X = Me, Et, Bz) point to the anionic chromophore $\text{Re(CO)}_3\text{(iPr-DAB)}^{-}$ with the bound X$^+$ ligand.\(^{(17)}\)

$[\text{Mn(Me)(CO)}_3\text{(iPr-DAB)}]^{-} \rightarrow [\text{Mn}(\text{CO)}_3\text{(iPr-DAB)}]^{\text{-}} + \text{Me}^+$ (9)

Notably, both complexes $[\text{Mn(X)(CO)}_3\text{(iPr-DAB)}]^{\text{2-}}$ (X = Me, Bz) are oxidized significantly more negatively than $[\text{Mn(Br)(CO)}_3\text{(iPr-DAB)}]^{\text{2-}}$ (see Table 2). According to a DFT-MO study\(^{(5)}\) of the model complex $[\text{Mn(Cl)(CO)}_3\text{(H-DAB)}]$, the oxidation of $[\text{Mn(Br)(CO)}_3\text{(iPr-DAB)}]^{\text{2-}}$ is largely localized on the p$_x$(Br) - d$_z$(Mn) HOMO (highest occupied molecular orbital) with a dominant contribution from the Br ligand. In contrast, the oxidation of the complex $[\text{Mn(Me)(CO)}_3\text{(iPr-DAB)}]^{\text{2-}}$ is localized on the HOMO possessing a d$_x$(Mn) character.\(^{(7)}\) The a(Mn- Me) bonding orbital then lies ca. 1 eV below the HOMO. On the other hand, the HOMO of $[\text{Mn(Bz)(CO)}_3\text{(iPr-DAB)}]^{\text{2-}}$ is a a$_x$(Mn-Bz) orbital.\(^{(7)}\) This apparent difference in the HOMO characters make the evaluation of the above $E_{\text{pa}}$ trends rather difficult. The irreversible oxidation was not investigated in detail.

**Discussion**

(Spectro)electrochemical experiments described herein point to a facile dissociation of the non-carbonyl axial ligand from the primary one-electron reduction products $[\text{Mn(Br)(CO)}_3\text{(iPr-DAB)}]^{-}$ and $[\text{Mn(X)(CO)}_3\text{(iPr-DAB)}]^{-}$ at X = THF, MeCN, nPrCN, P(OMe)$_3$. The (spectro)electrochemical experiments described herein point to a facile dissociation of the non-carbonyl axial ligand from the primary one-electron reduction products $[\text{Mn(Br)(CO)}_3\text{(iPr-DAB)}]^{-}$ and $[\text{Mn(X)(CO)}_3\text{(iPr-DAB)}]^{-}$ at X = THF, MeCN, nPrCN. These radical species could not be observed, even at 190 K and at ultrafast voltammogram scans. We have, however, shown that the transient 18e radicals $[\text{Mn(X)(CO)}_3\text{(iPr-DAB)}]^{\text{2-}}$ (X = donor solvent) are definitely involved in the reoxidation path of the ultimate two-electron reduction product $[\text{Mn(CO)}_3\text{(iPr-DAB)}]^{-}$ (see Scheme 1). Any reverse uptake of X by the transient radicals $[\text{Mn(X)(CO)}_3\text{(iPr-DAB)}]^{\text{2-}}$ along the reduction path is prevented by their instantaneous one-
The axial ligand X from [Mn(X)(CO)3(iPr-DAB)] (iPr-DAB) remains bound rather firmly at low temperatures, and therefore, these radicals are detectable in the electrolyzed solution.

In contrast to [Mn(X)(CO)3(iPr-DAB)]−, the corresponding Re complexes are significantly more stable. A similar conclusion can be drawn for other Mn and Re derivatives containing basic α-diamine ligands.Independent of the metal, the unpaired electron in these six-coordinate radicals is mainly localized on the lowest π*(α-diamine) orbital. The very close π(α-diamine) wavenumbers of the radicals [Mn(X)(CO)3(α-diamine)]− (M = Mn, Re; X = PR3, P(OR)3) reflect comparable M → CO π-back-donation and, hence, a similar distribution of the electron density within the (CO)3M(α-diamine) fragment. The more efficient dissociation of the axial ligand X from [Mn(X)(CO)3(iPr-DAB)]− relative to [Re(X)(CO)3(iPr-DAB)]− may arise from a larger electron delocalization between the singly occupied π*(α-diamine) and the π*(Mn-X) (i.e., combined p2(X) and pπ*(Mn)) orbitals, resulting in a stronger repulsion between the Mn center and the ligand X. The positive π−−π* overlap is assumed to increase substantially during an asymmetric distortion of [Mn(X)(CO)3(iPr-DAB)]− caused by an asymmetric stretching vibration of the radical complexes along the axial Mn−X bond. The stronger π−−π* interaction in the case of the radical Mn complexes may have its origin in the lower-lying and less diffuse σ*(Mn−X) orbital compared to that of σ*(Re−X).

The ECEC (reduction path of [Mn(X)(CO)3(iPr-DAB)]− (n = 0, X = Br; n = +1, X = THF, MeCN, nPrCN), analysed in detail in the Results (Scheme 1), is not unusual in organometallic electrochemistry. Suitable examples are the reduction of [Fe(X)(CO)3]− (X = C3H5, C4H5Me, CH3Br) (X = Cl, Br, I)43 and Fe(CO)5 or Cr(CO)6, studied in detail by Amatore et al. The common event along their reduction paths is generation of electron-deficient radicals whose dimerization cannot compete with their instantaneous reduction. Notably, a difference exists between the oxidation pathways of the two-electron reduction products [Fe(CO)5]2−/Fe(CO)5 and [Mn(CO)3(iPr-DAB)]+. The one-electron-oxidized coordinatively unsaturated 17-electron radicals [Fe(CO)5]− and [Cr(CO)5]− directly dimerize. In contrast, the five-coordinate radicals [Mn(CO)3(iPr-DAB)]+ have the odd electron localized on the iPr-DAB ligand10,40 and should, therefore, be defined as formally 16-electron species Mn−(CO)3(iPr-DAB)+. Their direct dimerization is, therefore, a rather complex process which apparently cannot compete efficiently with the alternative ECEC route to [Mn(CO)3(iPr-DAB)]− depicted in Scheme 1.

No significant difference was observed between the reduction paths of [Mn(X)(CO)3(NPPr)]− (X = Me, Bz).

Their lower reduction potentials relative to those of the other title complexes studied (see Table 2) reveal that the radical π*(iPr-DAB) LUMO (lowest unoccupied molecular orbital) of these complexes becomes considerably destabilized by coordination of the alkyl ligands. Regardless this trend, the one-electron-reduced products [Mn(X)(CO)3(iPr-DAB)]− (X = Me, Bz) are apparently more stable than, e.g., [Mn(Br)(CO)3(iPr-DAB)]−, as the radical anion with X = Me could even be detected by slow cyclic voltammetry. This difference is probably caused by a much higher energy of the π*(Mn−Me) orbital relative that of π*(Mn−Br), resulting in a weaker repulsive π*(Mn−Me)−π*(Mn−Me) interaction. The existence of the radical anionic intermediate along the reduction path leading directly to [Mn(CO)3(iPr-DAB)]− (see eq 9) excludes the dissociation of the Mn π radical via the intramolecular dissociative electron-transfer reaction introduced by Savéant46 on the model reaction R−X + e− → R+ + X− (R−X = alkyl halide).

**Bonding Properties of [Mn(CO)3(iPr-DAB)]− and Comparison with [Mn(CO)3(DBCat)]+.** The ultimate closed-shell two-electron reduction product [Mn(CO)3(iPr-DAB)]− is closely related to the five-coordinate anion [Mn(CO)3(DBCat)].47 (DBCat is defined in ref 14). DFT-MO calculations performed on the model compounds [Mn(CO)3(H-DAB)]− and [Mn(CO)3(H-Cat)]− confirm that substitution of the catecholate ligand by formally [iPr-DAB]− with a considerably higher π* level results in strongly changed HOMO and LUMO characters. The lowest electronic transition of [Mn(CO)3(H-Cat)]− possesses a significant HCat → Mn LMCT character whereas that of [Mn(CO)3(H-DAB)]− is largely delocalized, π(Mn−DAB) → π*(Mn−DAB), with a rather limited charge-transfer character. This transition in [Mn(CO)3(iPr-DAB)]− occurs at 490 nm, in agreement with 505 nm calculated for [Mn(CO)3(H-DAB)]−. The DFT data also document that the negative charge on [Mn(CO)3(iPr-DAB)]− is almost equally divided over the CO and iPr-DAB ligands, in contrast to [Mn(CO)3(DBCat)]− where it mainly resides on the DBCat ligand.47,49 This difference explains the considerably lower π(CO) wavenumbers of [Mn(CO)3(iPr-DAB)]− (see Table 2) in comparison with 1994 and 1891 (br) cm−1 for the latter anion (in THF).47 The effective oxidation-state distribution in the five-coordinate anion is best described as [(Mn(CO)3)3(iPr-DAB)−], with the Mn center bearing a partial positive charge. In contrast, the anion [Mn(CO)3(DBCat)]− is a less π-delocalized, formally Mn(DBCat−1) complex, which corresponds with its DBCat-localized one-electron oxidation, large π(CO) wavenumbers, and tendency to reversibly form six-coordinate adducts with various Lewis bases.47,50

**Relation between Electrochemical and Photochemical Generation of [Mn(CO)3(a-dimine)]−.** The photochemical formation of the five-coordinate

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(45) Wilms, M. P. unpublished results. According to DFT MO calculations on the model complex [MnEt(CO)(H-DAB)], the reduction of [Mn(X)(CO)3(iPr-DAB)]− (X = Me, Bz) is localized on a LUMO possessing a predominant π*(iPr-DAB) character with a small contribution from the alkyl ligand.
anions \([\text{Mn}(\text{CO})_3(\text{diimine})]^-\) (\(\text{diimine} = \text{bpy}, \text{iPr-DAB}\)) from fac-[\text{Mn}(\text{X})(\text{CO})_3(\text{diimine})] (X = \text{Br}) proceeds via several intermediates, including mer-[\text{Mn}(\text{Br})(\text{CO})_3(\text{diimine})] which further photodecomposes to reactive radicals \([\text{Mn}(\text{CO})_3(\text{diimine})]^+\) and \(\text{Br}^-\). Notably, irradiation of mer-[\text{Mn}(\text{Br})(\text{CO})_3(\text{diimine})] does not produce any carbonyl species.\(^6\)

The radicals \([\text{Mn}(\text{CO})_3(\text{diimine})]^+\) are the key transients which link together the photochemical and electrochemical routes to \([\text{Mn}(\text{CO})_3(\text{diimine})]^+\) (see Scheme 3). A fraction of photogenerated \([\text{Mn}(\text{CO})_3(\text{diimine})]^+\) can take up a solvent molecule. This process occurs even at room temperature, in agreement with the reoxidation path in Scheme 1. At \(T = 135\,\text{K}\) this uptake remains the only possibility\(^10\) as no dimer \([\text{Mn}(\text{CO})_3(\text{diimine})]_2\) was photochemically produced under such conditions.\(^4\) In toluene, the radicals \([\text{Mn}(\text{CO})_3(\text{R-DAB})]^+\) could be detected by EPR spectroscopy at \(T = 200 - 250\,\text{K}\).\(^{10,40}\) This experimental evidence allows us to safely conclude that the \([\text{Mn}(\text{CO})_3(\text{diimine})]^+\) photoproduct originates from an electron transfer from the six-coordinate \([\text{Mn}(\text{X})(\text{CO})_3(\text{diimine})]^+\) (X = donor solvent) to the five-coordinate \([\text{Mn}(\text{CO})_3(\text{diimine})]^+\) radicals present simultaneously in the solution (see Scheme 3). This disproportionation step is the characteristic event in the electrochemical DISP 1 sequence operating in the bulk solution (see eq 7). Importantly, in the presence of excess \(\text{PR}_3\), the inherently stable 18e radicals \([\text{Mn}(\text{PR})_3(\text{CO})_3(\text{diimine})]^+\) are the only photoproducts at low temperatures.\(^4\) Furthermore, the yield of \([\text{Mn}(\text{CO})_3(\text{diimine})]^+\) is negligible in very weakly coordinating toluene.\(^4\) The photochemical disproportionation route to \([\text{Mn}(\text{CO})_3(\text{diimine})]^+\) apparently cannot operate under these circumstances.

The second disproportionation product \([\text{Mn}(\text{X})(\text{CO})_3(\text{diimine})]^+\) (X = 2-MeTHF) probably converts back to parent fac-[\text{Mn}(\text{Br})(\text{CO})_3(\text{diimine})] via a substitution reaction with Br\(^-\), in analogy with the oxidation path in Scheme 1. It still remains unclear, however, how the primarily produced Br\(^-\) radicals transform to the corresponding anions. Recall that neither Br\(^+\) nor Br\(_2\) were actually detected on irradiation of mer-[\text{Mn}(\text{Br})(\text{CO})_3(\text{diimine})]\(^4\).

At \(T \geq 170\,\text{K}\), photochemically produced \([\text{Mn}(\text{CO})_3(\text{diimine})]^+\) thermally convert into the dimer \([\text{Mn}(\text{CO})_3(\text{diimine})]_2\). This is probably caused by the coupling reaction of the anions with unreacted parent fac-[\text{Mn}(\text{Br})(\text{CO})_3(\text{diimine})], introduced here in Scheme 1. For \(\text{diimine} = \text{iPr-DAB}\), we have shown that this reaction becomes largely inhibited already at \(T \leq 200\,\text{K}\), whereas lower temperatures are required for \(\text{diimine} = \text{bpy}\).\(^13\)

**Conclusions**

The detailed knowledge of the redox paths of the title complexes fac-[\text{Mn}(\text{X})(\text{CO})_3(\text{iPr-DAB})](n = 0, 1) and of the two-electron reduction product \([\text{Mn}(\text{CO})_3(\text{iPr-DAB})]^-\) provides an indispensable aid for the correct description of the electron-transfer events in the overall mechanism of the photochemical transformation of fac- and mer-[\text{Mn}(\text{Br})(\text{CO})_3(\text{diimine})] into \([\text{Mn}(\text{CO})_3(\text{iPr-DAB})]^-\) and/or \([\text{Mn}(\text{CO})_3(\text{iPr-DAB})]_2\).

The key electro- and photochemical transients are the five-coordinate radicals \([\text{Mn}(\text{CO})_3(\text{diimine})]^+\) whose redox behavior and reactivity toward Lewis bases markedly differ from those of the corresponding Re derivatives. The ultimate photo and reduction product \([\text{Mn}(\text{CO})_3(\text{iPr-DAB})]^-\) can be considered as a strongly \(\pi\)-delocalized five-coordinate complex with the negative charge divided over the CO and iPr-DAB ligands.

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**Supporting Information Available:** Figures 4, 6, 7B, and 9, showing IR spectra recorded during the reduction of \([\text{Mn}(\text{MeCN})(\text{CO})_3(\text{iPr-DAB})]^+\) at 198 K, cyclic voltammograms of \([\text{Mn}(\text{Br})(\text{CO})_3(\text{iPr-DAB})]^+\) (in THF) and \([\text{Mn}(\text{MeCN})(\text{CO})_3(\text{iPr-DAB})]^+\) (in THF); and \(E_v\) vs log(\(v\)) and \(E_{p1/2}\) vs log(\(v\)) functions of \([\text{Mn}(\text{X})(\text{CO})_3(\text{iPr-DAB})]^+\) (n = 0, X = Br; n = +1, X = THF), respectively (4 pages). Ordering information is given on any current masthead page.

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