

*Manganese tricarbonyl complexes with asymmetric 2 2-iminopyridine ligands: toward decoupling steric and electronic 3 factors in electrocatalytic CO<sub>2</sub> reduction*

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# Manganese Tricarbonyl Complexes with Asymmetric 2-Iminopyridine Ligands: Toward Decoupling Steric and Electronic Factors in Electrocatalytic CO<sub>2</sub> Reduction

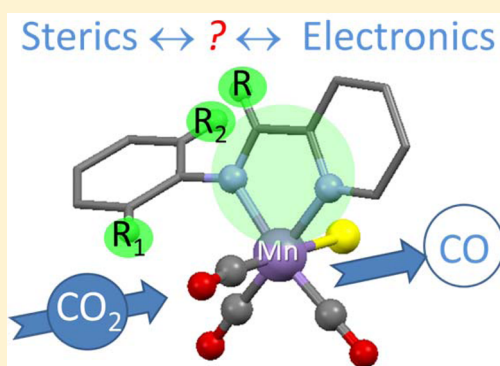
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**S** Supporting Information

**ABSTRACT:** Manganese tricarbonyl bromide complexes incorporating IP (2-(phenylimino)pyridine) derivatives, [MnBr(CO)<sub>3</sub>(IP)], are demonstrated as a new group of catalysts for CO<sub>2</sub> reduction, which represent the first example of utilization of (phenylimino)pyridine ligands on manganese centers for this purpose. The key feature is the asymmetric structure of the redox-noninnocent ligand that permits independent tuning of its steric and electronic properties. The  $\alpha$ -diimine ligands and five new Mn(I) compounds have been synthesized, isolated in high yields, and fully characterized, including X-ray crystallography. Their electrochemical and electrocatalytic behavior was investigated using cyclic voltammetry and UV–vis–IR spectroelectrochemistry within an OTTLE cell. Mechanistic investigations under an inert atmosphere have revealed differences in the nature of the reduction products as a function of steric bulk of the ligand. The direct ECE (electrochemical–chemical–electrochemical) formation of a five-coordinate anion [Mn(CO)<sub>3</sub>(IP)]<sup>−</sup>, a product of two-electron reduction of the parent complex, is observed in the case of the bulky DIPIMP (2-(((2,6-diisopropylphenyl)imino)methyl)pyridine), TBIMP (2-(((2-*tert*-butylphenyl)imino)methyl)pyridine), and TBIEP (2-(((2-*tert*-butylphenyl)imino)ethyl)pyridine) derivatives. This process is replaced for the least sterically demanding IP ligand in [MnBr(CO)<sub>3</sub>(IMP)] (2-((phenylimino)methyl)pyridine) by the stepwise formation of such a monoanion via an ECEC(E) mechanism involving also the intermediate Mn–Mn dimer [Mn(CO)<sub>3</sub>(IMP)]<sub>2</sub>. The complex [MnBr(CO)<sub>3</sub>(IPIMP)] (2-(((2-diisopropylphenyl)imino)methyl)pyridine), which carries a moderately electron donating, moderately bulky IP ligand, shows an intermediate behavior where both the five-coordinate anion and its dimeric precursor are jointly detected on the time scale of the spectroelectrochemical experiments. Under an atmosphere of CO<sub>2</sub> the studied complexes, except for the DIPIMP derivative, rapidly coordinate CO<sub>2</sub>, forming stable bicarbonate intermediates, with no dimer being observed. Such behavior indicates that the CO<sub>2</sub> binding is outcompeting another pathway: *viz.*, the dimerization reaction between the five-coordinate anion and the neutral parent complex. The bicarbonate intermediate species undergo reduction at more negative potentials (ca. −2.2 V vs Fc/Fc<sup>+</sup>), recovering [Mn(CO)<sub>3</sub>(IP)]<sup>−</sup> and triggering the catalytic production of CO.



The interest in solar fuels in terms of both photocatalytic and electrocatalytic CO<sub>2</sub> reduction,<sup>1</sup> in the latter case utilizing sustainable electricity, has been increasing markedly in the new millennium. The recent demonstration of the electrocatalytic activity of manganese<sup>2</sup> analogues of the archetypal Re(I) catalysts<sup>3–6</sup> for CO<sub>2</sub> reduction has given a new impetus to research into noble-metal-free catalytic systems. [MnBr(CO)<sub>3</sub>( $\alpha$ -diimine)] complexes have been shown to outperform rhenium-based analogues with regard to CO<sub>2</sub> reduction under certain conditions.<sup>7</sup> Most notably, the presence of a Brønsted acid<sup>7–10</sup> appears to be a prerequisite for catalysis with a range of tricarbonyl Mn  $\alpha$ -diimine complexes.

Mechanistic studies<sup>5,10</sup> of the active 2,2'-bipyridine-based (R-bpy) manganese catalysts have shown that one-electron reduction of the parent complex [MnBr(CO)<sub>3</sub>(R-bpy)]

precursor results in the formation of the Mn–Mn dimer<sup>50</sup> [Mn(CO)<sub>3</sub>(R-bpy)]<sub>2</sub>.<sup>8,9</sup> Notably, neither the primary reduction product [MnBr(CO)<sub>3</sub>(R-bpy)<sup>•−</sup>] nor the five-coordinate radical intermediates [Mn(CO)<sub>3</sub>(R-bpy)]<sup>•</sup> have been detected by either UV–vis or IR spectroscopy.<sup>2,7</sup> Nanosecond time-resolved infrared (TRIR) studies reveal that no detectable solvent adduct is formed before the dimerization of Mn species on this time scale; instead, the five-coordinate species is observed, which rapidly dimerizes.<sup>10</sup> For some of the Re analogues, a one-electron-reduced complex, [ReCl(CO)<sub>3</sub>(R-bpy)<sup>•−</sup>], was observed by IR spectroscopy and identified by the ca. 15–20 cm<sup>−1</sup> decrease in the  $\tilde{\nu}(\text{CO})$  energy,<sup>11–13</sup> as was the 61

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62 five-coordinate radical  $[\text{Re}(\text{CO})_3(\text{tBu-bpy})]^\bullet$  by an additional  
63  $15\text{--}20\text{ cm}^{-1}$  shift.

64 Two mechanisms have been proposed<sup>10,14–18</sup> for the  
65 ultimate reduction of  $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})]_2$  in the presence  
66 of  $\text{CO}_2$ , which can be referred to as the anionic and the  
67 oxidative addition<sup>19</sup> pathways. The anionic pathway involves  
68 reduction of the dimer  $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})]_2$  at a potential  
69 more negative than that of the parent complex, generating the  
70 five-coordinate anion  $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})]^-$ , to which  $\text{CO}_2$   
71 coordinates and is catalytically reduced in the presence of a  
72 Brønsted acid (the source of  $\text{H}^+$ ). The anionic pathway is  
73 broadly similar to the two-electron pathway observed for Re  
74 complexes.<sup>20,21</sup> In contrast, the uncommon second pathway  
75 identified using pulsed EPR studies<sup>19</sup> involves coordination of  
76  $\text{CO}_2$  to the dimer  $[\text{Mn}(\text{CO})_3(2,2'\text{-bpy})]_2$  in the presence of a  
77 Brønsted acid in a concerted oxidative addition step. This  
78 process is shown to generate a low-spin  $\text{Mn}^{\text{II}}\text{--COOH}$  complex,  
79 from which CO is subsequently released.

80 Since the catalytic  $\text{CO}_2$  reduction with the use of  
81  $[\text{MnX}(\text{CO})_3(\alpha\text{-diimine})]$  ( $\alpha\text{-diimine} = \text{R-bpy}$ ;  $\text{X} = \text{halide}$  or  
82 pseudohalide) has been shown to proceed in many cases via a  
83 dimerization step, immobilization of the catalyst<sup>22</sup> or  
84 introduction of sterically hindering groups at bpy may have a  
85 profound effect on the catalytic activity.<sup>23</sup> Indeed, it has  
86 recently been shown that the use of bipyridines incorporating  
87 bulky groups in the 6,6'-positions<sup>24,25</sup> (or another bulkier  
88 heterocyclic ligand<sup>26</sup>) largely inhibits dimerization in the  
89 catalytic cycle. The result is the formation of the stable five-  
90 coordinate anion via the two-electron transfer (ECE) at the first  
91 cathodic wave. However, coordination of  $\text{CO}_2$  to the five-  
92 coordinate anion produces a stable species which must be  
93 reduced at considerably more negative potentials<sup>27</sup> in order for  
94 catalysis to be observed. It has recently been shown that in the  
95 presence of a Lewis acid,  $\text{Mg}^{2+}$ ,<sup>7,28</sup> the catalytic overpotential<sup>29</sup>  
96 is decreased by approximately 400 mV.

97 A similar behavior was observed for  $[\text{MnBr}(\text{CO})_3(\text{R-DAB})]$   
98 complexes featuring nonaromatic 1,4-diazabuta-1,3-diene (R-  
99 DAB)<sup>8,9,30</sup> ligands. The reduction potentials of the dimers  
100  $[\text{Mn}(\text{CO})_3(\text{R-DAB})]_2$  are almost identical with those of the  
101 parent complexes, implying that the five-coordinate anion is  
102 produced directly upon reduction and reacts readily with  $\text{CO}_2$   
103 in solution to form a stable bicarbonate complex<sup>8,30</sup> and, as  
104 with sterically hindered 2,2'-bipyridine ligands,<sup>25</sup> a much more  
105 negative potential (below 2 V vs  $\text{Fc}/\text{Fc}^+$ ) must be applied to  
106 trigger catalytic  $\text{CO}_2$  reduction. Functionalization of the  $\alpha$ -  
107 diimine with a sterically bulky group such as <sup>t</sup>Bu should also  
108 modify the electronic properties of the ligand. In particular, this  
109 change should affect the energy of the LUMO, the reduction  
110 potential, and catalytic activity.<sup>23–33</sup>

111 Introducing steric bulk<sup>23,25</sup> to prevent unwanted reactions of  
112 the catalytic species, including dimerization as either Mn–Mn<sup>9</sup>  
113 or C(imino)–C(imino) bound species,<sup>21</sup> while at the same  
114 time reducing the risk of increased overpotential is a  
115 challenging task. Molecular designs that allow for steric and  
116 electronic effects to be decoupled are required.

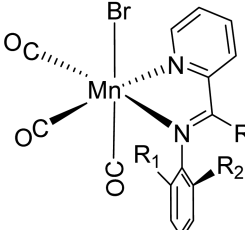
117 In this paper we have investigated a family of tricarbonyl  
118 manganese complexes featuring asymmetric  $\alpha$ -diimine ligands,  
119 iminopyridines (IP).<sup>21,23,34,35</sup> They combine an accessible  
120  $\text{C}=\text{N}$  imino bond of the diazabuta-1,3-diene derivatives  
121 DAB<sup>32</sup> with the aromatic pyridine part, thereby being a  
122 “hybrid” of 2,2'-bipyridine ligands and nonaromatic R-DAB  
123 ligands. Each of the parts is important: for instance, a Mn(I)  
124 complex with Ph-DAB demonstrates formation of five-

coordinate anions, with the steric bulk of the ligand preventing  
125 dimerization, but does not act as a catalyst for  $\text{CO}_2$  reduction  
126 due to insufficiently negative reduction potential.<sup>8</sup>

127 Introduction of the pyridine moiety allows one to reach the  
128 required reduction potentials, while the Ph group attached to the  
129  $\text{C}=\text{N}$  fragment can be decorated with sterically demanding  
130 substituents, ensuring steric bulk while only slightly affecting  
131 the electronic properties. As the phenyl moiety lies out of plane  
132 with the conjugated  $\alpha$ -diimine (because of steric effects), the  $\pi$   
133 electrons of the phenyl substituent are decoupled from the  
134 metallacycle formed by the metal center and the  $\alpha$ -diimine.  
135 Therefore, functionalization of the phenyl ring in the R<sub>1</sub> and R<sub>2</sub>  
136 positions with large sterically hindering groups (that also have a  
137 +I effect) will have only very minimal effects on the electronics  
138 of the active site of the molecule (vide infra). These ligands  
139 offer an opportunity to separate steric and electronic effects in a  
140 chelating  $\alpha$ -diimine ligand to a certain extent. Thus, the  
141 possibility arises of a systematic variation of the steric hindrance  
142 by changing R<sub>1</sub> and R<sub>2</sub> groups, while the R group strongly  
143 influences the electronics (but could also hinder the  $\text{C}=\text{N}$   
144 bond).

145 These ligands are readily accessible via simple synthetic  
146 routes, which are suitable for the purpose of comparatively  
147 independent alteration of steric and electronic effects (Chart 1).  
148 c1

Chart 1. General Structure of the Complexes with the Asymmetric  $\alpha$ -Diimine Ligands (2-R<sub>1</sub>-6-R<sub>2</sub>-phenyl)(R-imino)pyridine<sup>a</sup>



Ligand	R	R <sub>1</sub>	R <sub>2</sub>
IMP (1)	H	H	H
IPIMP (2)	H	<sup>i</sup> Pr	H
DIPIMP (3)	H	<sup>i</sup> Pr	<sup>i</sup> Pr
TBIMP (4)	H	<sup>t</sup> Bu	H
TBIEP (5)	CH <sub>3</sub>	<sup>t</sup> Bu	H

<sup>a</sup>Numbers given in parentheses correspond to the Mn complexes. When R = H, the ligands will be derivatives of [(phenylimino)methyl]pyridine: IMP (R<sub>1,2</sub> = H), IPIMP (R<sub>1</sub> = <sup>i</sup>Pr, R<sub>2</sub> = H), and DIPIMP (R<sub>1,2</sub> = <sup>i</sup>Pr), TBIMP (R<sub>1</sub> = <sup>t</sup>Bu, R<sub>2</sub> = H). R = CH<sub>3</sub> gives TBIEP, [((*tert*-butylphenyl)imino)ethyl]pyridine.

The potential of such ligands<sup>34–38</sup> has been convincingly  
149 illustrated by the recent work on a Re tricarbonyl complex with  
150 2-[(2-cyclohexyl-1-methyl)methyl]imino]pyridine<sup>36</sup> (both the  
151 one-electron-reduced parent complex and the neutral five-  
152 coordinate Re(0) species were detected), and Mo pyridine-  
153 monoimides.<sup>34</sup>

154 Herein we report a new series of manganese-based catalysts  
155 for  $\text{CO}_2$  reduction. We will show that a change in the structure  
156 of the ligands within the same series affects the efficiency of the  
157 process and the relative distribution of the intermediate species,  
158 demonstrating the versatile and tunable nature of these types of  
159 catalysts.  
160

## EXPERIMENTAL SECTION

161 All solvents were supplied by VWR and used as received. The  
162 compounds were purchased from either Sigma-Aldrich or Strem  
163 Chemicals and, unless stated, used as received. Tetrabutylammonium  
164 hexafluorophosphate,  $[\text{Bu}_4\text{N}][\text{PF}_6]$ , was recrystallized from hot  
165 ethanol and dried overnight in a vacuum oven before use in the  
166 electrochemical studies. TBIEP (2-[(2-*tert*-butylphenyl)imino]ethyl]-  
167



168 pyridine) and TBIMP were synthesized as previously described;<sup>35</sup> the  
169 analytical data matched those reported previously. Unless otherwise  
170 stated, UV–vis spectra were recorded on a Carry 50 Bio  
171 spectrophotometer and IR spectra on a PerkinElmer Spectrum 1  
172 FT-IR spectrometer.

173 **Syntheses.** *IMP* (2-[(Phenylimino)methyl]pyridine). Aniline (11.3  
174 mmol, 1.05 g, 1.02 mL) was added to 2-pyridinecarboxaldehyde (11.3  
175 mmol, 1.2 g, 1.1 mL) in flame-dried glassware and stirred for 1 h.  
176 Hexane (10 mL) was added and the solution dried over sodium  
177 sulfate. The solution was filtered, concentrated under vacuum, and  
178 placed in a freezer overnight. The large yellow needlelike crystals that  
179 formed were filtered and washed with hexane. Yield: 73%. <sup>1</sup>H NMR  
180 (400 MHz, CDCl<sub>3</sub>): δ 8.72 (d, *J* = 4.7 Hz, 1H), 8.61 (s, 1H), 8.21 (d, *J*  
181 = 7.9 Hz, 1H), 7.83 (td, *J* = 7.7, 1.6 Hz, 1H), 7.47–7.35 (m, 3H), 7.29  
182 (d, *J* = 7.7 Hz, 3H), 1.58 (s, 4H).

183 *IPIMP* (2-[2-((Isopropylphenyl)imino)methyl]pyridine). 2-Isopro-  
184 pyraniline (12.4 mmol, 1.7 g, 1.8 mL) was mixed with 2-  
185 pyridinecarboxaldehyde (12.4 mmol, 1.3 g, 1.2 mL) in flame-dried  
186 glassware and stirred for 1 h. Hexane (20 mL) was added and the  
187 solution dried over sodium sulfate. The solution was filtered and  
188 solvent removed under vacuum, yielding the product as a brown oil.  
189 Previous reports indicated that this compound could not be  
190 crystallized; therefore, the oil was used in the next reaction step  
191 without further purification (purity by NMR >97%). <sup>1</sup>H NMR (400  
192 MHz, CDCl<sub>3</sub>): δ 8.72 (ddd, *J* = 4.8, 1.6, 0.9 Hz, 1H), 8.54 (s, 1H),  
193 8.26 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.82 (ddd, *J* = 7.9, 1.7, 0.8 Hz, 1H),  
194 7.45–7.32 (m, 2H), 7.31–7.22 (m, 2H), 7.08–6.96 (m, 1H), 3.56 (dp,  
195 *J* = 13.8, 6.8 Hz, 1H), 1.26 (dd, *J* = 6.8, 4.1 Hz, 7H).

196 *DIPIMP* (2-[(2,6-Diisopropylphenyl)imino)methyl]pyridine). 2,6-  
197 Diisopropylaniline (11.3 mmol, 2 g, 2.1 mL) was mixed with 2-  
198 pyridinecarboxaldehyde (11.3 mmol, 1.2 g, 1.1 mL) in flame-dried  
199 glassware and stirred for 2 h. Hexane (10 mL) was added and the  
200 solution dried over sodium sulfate. The solution was filtered and  
201 concentrated before being placed in a freezer overnight. Light brown  
202 to yellow crystals were formed, which were filtered off and washed  
203 with hexane. Yield: 67%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.73 (ddd, *J*  
204 = 4.8, 1.7, 0.9 Hz, 1H), 8.31 (s, 1H), 8.27 (dt, *J* = 7.9, 1.0 Hz, 1H),  
205 7.90–7.82 (m, 1H), 7.42 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 7.22–7.07  
206 (m, 3H), 2.97 (hept, *J* = 6.9 Hz, 2H), 1.62 (s, 1H), 1.18 (d, *J* = 6.9 Hz,  
207 13H).

208 Complexes 1–6 were prepared from [MnBr(CO)<sub>5</sub>] and the  
209 corresponding ligand, using diethyl ether as a solvent. The products  
210 were collected by centrifugation and washed with diethyl ether to  
211 afford analytically pure 1–6. <sup>1</sup>H NMR spectra for 1–5 are given in  
212 Figure S122–S126 in the Supporting Information.

213 [MnBr(CO)<sub>5</sub>(IMP)] (1). [MnBr(CO)<sub>5</sub>] (1.1 mmol, 0.3 g) was  
214 combined with IMP (1.1 mmol, 0.2 g) in diethyl ether (20 mL) and  
215 refluxed under aerobic conditions for 4 h.<sup>39</sup> The product was formed  
216 in quantitative yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.26 (d, *J* = 5.0  
217 Hz, 1H), 8.45 (s, *J* = 27.9 Hz, 1H), 8.14–7.79 (m, 3H), 7.68–7.36 (m,  
218 5H). HRMS (TOF-ES, +ve): *m/z* (M + Na<sup>+</sup>) calcd for  
219 C<sub>15</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>NaBrMn 422.9153, found 422.9149.

220 [MnBr(CO)<sub>5</sub>(IPIMP)] (2). [MnBr(CO)<sub>5</sub>] (0.89 mmol, 0.24 g) was  
221 combined with IPIMP (0.89 mmol, 0.2 g) in diethyl ether (20 mL)  
222 and refluxed under aerobic conditions for 4 h. The product was  
223 formed in quantitative yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.27 (s,  
224 1H), 8.39 (s, 1H), 8.04 (s, 1H), 7.94 (d, *J* = 4.1 Hz, 1H), 7.78 (d, *J* =  
225 7.0 Hz, 1H), 7.61 (s, 1H), 7.48 (d, *J* = 15.3 Hz, 1H), 7.43 (d, *J* = 6.7  
226 Hz, 1H), 7.37 (t, 1H), 7.30 (d, *J* = 6.9 Hz, 1H), 3.58 (s, 1H), 3.03 (d, *J*  
227 = 35.6 Hz, 1H), 1.47–1.11 (m, 1H). HRMS (TOF-ES, +ve): *m/z* (M  
228 + Na<sup>+</sup>) calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>NaBrMn 464.9622, found 464.9644.

229 [MnBr(CO)<sub>5</sub>(DIPIMP)] (3). [MnBr(CO)<sub>5</sub>] (0.75 mmol, 0.2 g) was  
230 combined with DIPIMP (0.75 mmol, 0.2 g) in diethyl ether (20 mL)  
231 and refluxed under aerobic conditions for 4 h. The product was  
232 formed in 97% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.30 (s, 1H),  
233 8.41 (s, 1H), 7.99 (d, *J* = 50.7 Hz, 2H), 7.63 (s, 1H), 7.34 (s, 2H), 4.04  
234 (s, 1H), 2.91 (s, 1H), 1.34 (d, *J* = 3.1 Hz, 6H), 1.05 (dd, *J* = 80.6, 35.1  
235 Hz, 6H). HRMS (TOF-ES, +ve): *m/z* (M + Na<sup>+</sup>) calcd for  
236 C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>NaBrMn 507.0092, found 507.0107.

[MnBr(CO)<sub>5</sub>(TBIMP)] (4). [MnBr(CO)<sub>5</sub>] (0.84 mmol, 0.23 g) was  
237 combined with DIPIMP (0.84 mmol, 0.2 g) in diethyl ether (20 mL)  
238 and refluxed under aerobic conditions for 4 h. The product was  
239 formed in quantitative yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.27 (d, *J* =  
240 4.4 Hz, 1H), 8.50 (s, 1H), 8.12 (d, *J* = 6.9 Hz, 1H), 8.03 (t, *J* = 7.2  
241 Hz, 1H), 7.91 (d, *J* = 7.1 Hz, 1H), 7.61 (t, *J* = 6.2 Hz, 1H), 7.57 (d, *J* =  
242 7.4 Hz, 1H), 7.30 (t, 1H), 1.43 (s, 1H). HRMS (TOF-ESI, +ve): *m/z*  
243 (M + Na<sup>+</sup>) calcd for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>NaBrMn 478.9774, found 478.9789.

244 [MnBr(CO)<sub>5</sub>(TBIEP)] (5). [MnBr(CO)<sub>5</sub>] (0.8 mmol, 0.22 g) was  
245 combined with TBIEP (0.8 mmol, 0.2 g) and refluxed under aerobic  
246 conditions in diethyl ether (20 mL) for 4 h. The product was formed  
247 in quantitative yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.28 (d, *J* = 5.0  
248 Hz, 1H), 8.04 (td, *J* = 7.8, 1.3 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.88  
249 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.65–7.54 (m, 2H), 7.34–7.27 (m, 2H),  
250 2.39 (s, 3H), 1.39 (s, 8H). HRMS (TOF-ES, +ve): *m/z* (M + Na<sup>+</sup>)  
251 calcd for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>NaBrMn 492.9935, found 492.9934.

252 [MnBr(CO)<sub>5</sub>(bpy)] (6). This compound was prepared following the  
253 literature procedure;<sup>2</sup> analytical data are in agreement with the  
254 literature data. [MnBr(CO)<sub>5</sub>] (1.28 mmol, 0.35 g) was combined with  
255 2,2'-bipyridine (1.28 mmol, 0.2 g) in diethyl ether (20 mL) and  
256 refluxed under aerobic conditions for 4 h. The product was formed in  
257 80% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.27 (d, *J* = 4.3 Hz, 1H),  
258 8.12 (d, *J* = 6.5 Hz, 1H), 7.99 (t, 1H), 7.53 (t, 1H). HRMS (TOF-ESI,  
259 +ve): *m/z* (M + Na<sup>+</sup>) calcd for C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>NaBrMn 396.8991, found  
260 369.8988.

261 **Cyclic Voltammetry.** Cyclic voltammetry was performed using a  
262 Princeton Applied Research VersaSTAT3 potentiostat on 2 mM 1–6  
263 in Grubbs dried HPLC-grade acetonitrile containing 2 × 10<sup>-1</sup> M  
264 [Bu<sub>4</sub>N][PF<sub>6</sub>] as supporting electrolyte. A glassy-carbon working  
265 electrode (surface area 0.07 cm<sup>2</sup>, polished on alumina and paper)  
266 and a Pt-wire counter electrode were used with a 0.1 M KCl Ag/AgCl  
267 reference electrode.

268 The solutions were deoxygenated by bubbling thoroughly with  
269 bottled N<sub>2</sub> (BOC), and the N<sub>2</sub> atmosphere was maintained over the  
270 samples during the experiment. To test for catalytic current in the  
271 presence of CO<sub>2</sub>, the samples were bubbled thoroughly with bottled  
272 CO<sub>2</sub> (BOC) and cyclic voltammograms (CVs) were recorded under  
273 an atmosphere of CO<sub>2</sub> (some residual water might be present in the  
274 CO<sub>2</sub> used to saturate the samples). Water was then added (0.3–6 mL  
275 of the solution of each sample) to test the effects of Brønsted acid.  
276 Ferrocene was added as the internal standard at the end of all  
277 experiments.

278 **Spectroelectrochemistry.** Infrared spectroelectrochemistry was  
279 performed using an EmStat3 or EmStat3+ potentiostat (PalmSens,  
280 Houten, The Netherlands). The solution of 4 mM complex in the  
281 presence of 3 × 10<sup>-1</sup> M [Bu<sub>4</sub>N][PF<sub>6</sub>] in dry acetonitrile was analyzed  
282 using an optically transparent thin-layer electrochemical (OTTLE) cell  
283 equipped with Pt minigrid working and auxiliary electrodes, an Ag-  
284 microwire pseudoreference electrode, and CaF<sub>2</sub> windows. Samples  
285 were prepared under an argon atmosphere; for electrocatalytic  
286 measurements, the solutions were bubbled with CO<sub>2</sub> on a frit (a  
287 few minutes) to saturation under normal pressure. Parallel IR and  
288 UV–vis spectral monitoring during the spectroelectrochemical  
289 experiment was performed on a Bruker Vertex 70v FT-IR  
290 spectrometer or PerkinElmer Spectrum 1 and a Scinco S-3100  
291 spectrophotometer, respectively. Thin-layer CVs were recorded in the  
292 course of the experiment.

293 **Gas Chromatography Linked to Electrolysis.** Bulk electrolysis  
294 was performed on a 0.17 mM solution of each of the complexes in a 60  
295 mL solution of acetonitrile/water (9/1 v/v). The cell setup consisted  
296 of a Pt-mesh working electrode, a Pt-rod counter electrode in a  
297 semiporous compartment, and an Ag-wire pseudoreference electrode  
298 in a 0.1 M KCl solution. The potential of the Fc/Fc<sup>+</sup> recorded in this  
299 setup using a glassy-carbon 3 mm diameter electrode was +0.350 V vs  
300 Ag wire pseudoreference. Hence, in order to reach the potential  
301 necessary for the CO<sub>2</sub> reduction as estimated from the CV data, the  
302 potential was held at -1.9 V vs Ag wire for all samples: i.e., -2.25 V vs  
303 Fc/Fc<sup>+</sup>. Prior to electrolysis, a CV was recorded in the bulk electrolysis  
304 cell using a glassy-carbon working electrode. Gas samples (100 μL)  
305 were withdrawn from the head space at regular intervals and analyzed 306

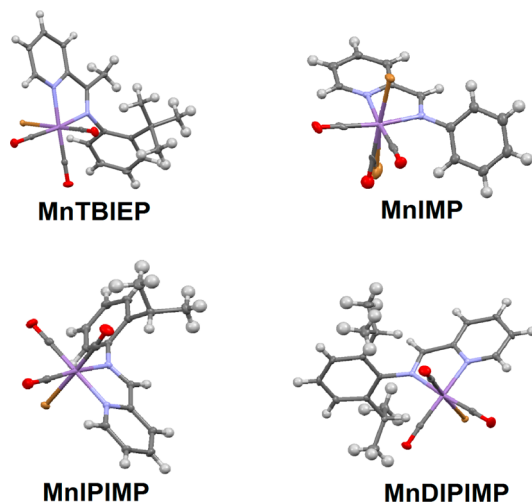
307 by a gas chromatograph fitted with a thermal conductivity detector  
308 (Perkin ElmerArnel autosystem XL). H<sub>2</sub> was used as the carrier gas in  
309 CO-quantification experiments. N<sub>2</sub> was used as a carrier gas in the  
310 control experiment.

311 **X-ray Crystallography.** Crystals were grown using the antisolvent  
312 crystallization method, with the solvent dichloromethane and hexane  
313 as the antisolvent. Single-crystal X-ray diffraction data were collected  
314 on a Bruker SMART APEX-II CCD diffractometer operating a Mo K $\alpha$   
315 sealed-tube X-ray source or a Bruker D8 Venture diffractometer  
316 equipped with a PHOTON 100 dual-CMOS chip detector and  
317 operating a Cu K $\alpha$  I $\mu$ S microfocuss X-ray source. The data were  
318 processed using Bruker APEX3 software and corrected for absorption  
319 using empirical methods (SADABS) based upon symmetry-equivalent  
320 reflections combined with measurements at different azimuthal  
321 angles.<sup>40</sup> The crystal structures were solved and refined using the  
322 Bruker SHELXTL software package.

323 **Computational Methods.** Density functional theory (DFT)  
324 calculations were performed using the Gaussian 09 program package.<sup>41</sup>  
325 All calculations utilized the global hybrid exchange correlation  
326 functional B3LYP,<sup>42,43</sup> a “mixed” basis set consisting of the SDD  
327 basis set as defined in Gaussian for Mn and the 6-311G(d,p) basis set  
328 for all other atoms.<sup>44–47</sup> The solvent acetonitrile was included using  
329 the polarizable continuum model (PCM) as implemented in  
330 Gaussian.<sup>48,49</sup> All species were modeled at the lowest multiplicity  
331 appropriate for the electron count, and the restricted formalism was  
332 used for closed-shell cases. An “ultrafine” integral grid, as defined by  
333 Gaussian, was used and all geometries were confirmed as minima by  
334 the absence of imaginary frequencies in their vibrational spectra as  
335 calculated within the harmonic approximation. The values of  
336 vibrational frequencies have been scaled by 0.966 to match  
337 experimental  $\nu(\text{CO})$  values of the parent neutral complexes.

## 338 ■ RESULTS AND DISCUSSION

339 **X-ray Crystallography.** The crystal structures of the  
340 complexes [MnBr(CO)<sub>3</sub>( $\alpha$ -diimine)] ( $\alpha$ -diimine = TBIEP,  
341 IMP, IPIMP, DIPIMP) are shown in Figure 1, and selected  
342 bond distances and angles are given in Table S11 in the  
343 Supporting Information. Similar bond lengths are observed for  
344 the four complexes, and these are in good agreement with  
345 related [MnBr(CO)<sub>3</sub>( $\alpha$ -diimine)] species reported in the  
346 literature. The X-ray data are in good agreement with the  
347 results obtained through DFT calculations. As predicted by



**Figure 1.** X-ray crystal structures of the studied complexes shown with thermal ellipsoids at the 50% probability level. CCDC 1457930 (MnTBIEP), 1457931 (MnDIPIMP), 1457932 (MnIPIMP), 1457933 (MnIMP). Full crystallographic details are given in the Supporting Information.

DFT, the pyridine and phenyl rings lie approximately 348  
orthogonally to one another (dihedral angles between the 349  
corresponding planes are MnTBIEP 84.55°, MnIPIMP 83.64°, 350  
MnDIPIMP 78°), resulting in little orbital overlap between 351  
these two moieties, with the exception of MnIMP, where the 352  
two ring systems were significantly less orthogonal (56.54°). 353

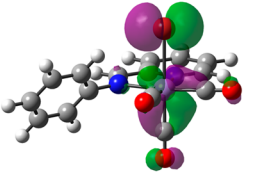
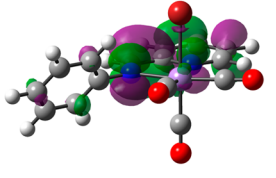
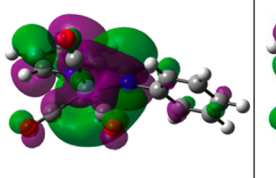
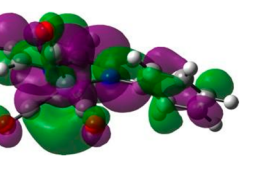
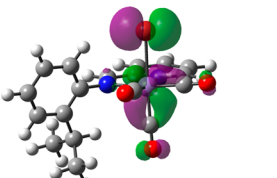
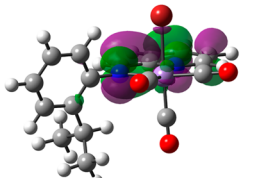
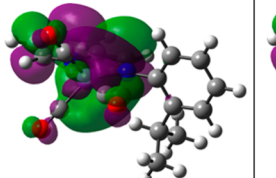
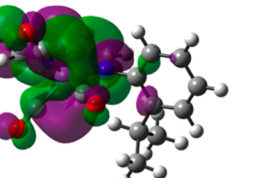
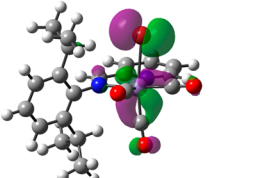
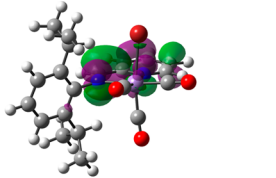
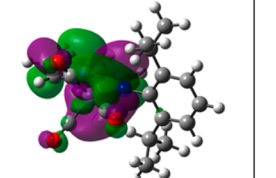
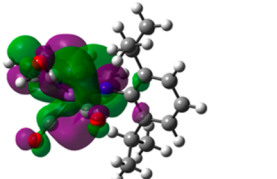
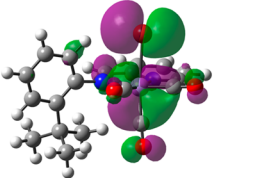
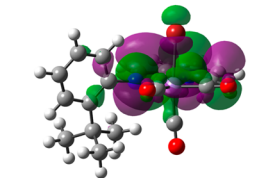
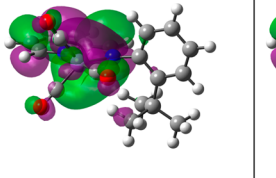
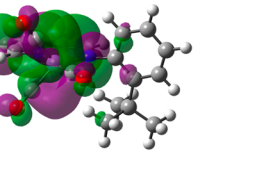
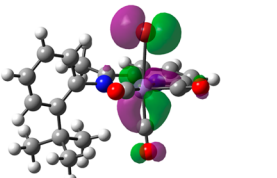
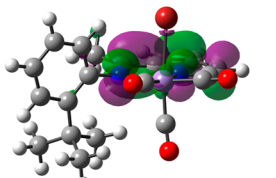
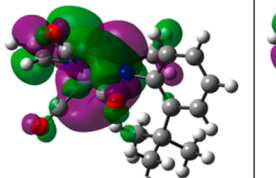
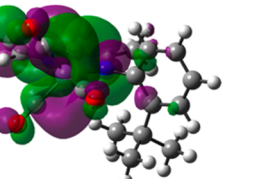
The crystal structures have revealed significant steric 354  
hindrance between the substituents R = Me and R<sub>1</sub> = <sup>t</sup>Bu in 355  
MnTBIEP, which inhibits rotation of the Ph ring and confers 356  
conformational rigidity. Rotation of the Ph ring in MnDIPIMP 357  
is also inhibited by the two <sup>i</sup>Pr groups and hence also has 358  
conformational rigidity. In contrast, MnIMP and MnIPIMP 359  
exhibit much smaller steric hindrance, facilitating the rotation of 360  
the phenyl ring. 361

**Computational Investigations of Molecular Structures 362  
and Frontier Orbitals by DFT.** The optimized geometries of 363  
the studied complexes with frontier orbitals overlaid as 364  
calculated by DFT are displayed in Table 1. As anticipated, 365  
the phenyl group lies out of the plane of the chelating diimine. 366  
The HOMO is localized predominantly over the axial Br–Mn– 367  
C(O) bonds with almost no contribution from the phenyl 368  
moiety. The LUMO resides largely on the imine, pyridyl, and 369  
metal center, with minimal contribution from the C1–C2 and 370  
C1–C6  $\sigma$  bonds of the phenyl groups. In the case of MnIMP, 371  
due to the lack of substitution at R<sub>1</sub> and R<sub>2</sub>, the phenyl moiety 372  
is less sterically hindered and thus is positioned closer to the 373  
plane of the imino-pyridine fragment, resulting in a small 374  
degree of involvement of the phenyl  $\pi$  system in the low-energy 375  
unoccupied orbitals. This trend continues in the other low- 376  
energy unoccupied orbitals (see Figures S11–S110 in the 377  
Supporting Information). 378

The energies of the HOMO in all complexes are within 0.02 379  
eV of each other, and all compounds in the IMP subset of 380  
complexes have a LUMO that lies within 0.03 eV of those of 381  
the other complexes. In contrast, MnTBIEP shows a difference 382  
in LUMO energy of +0.19 eV in comparison with IPIMP. This 383  
larger difference in LUMO energy comes as result of 384  
methylation at the R position. In contrast, adding two isopropyl 385  
groups at the R<sub>1</sub> and R<sub>2</sub> positions resulted in an energy 386  
difference of just 0.02 eV between MnIMP and MnDIPIMP. 387  
The results of the calculations on the trends in the energies of 388  
HOMO/LUMO are in full agreement with the experimentally 389  
determined redox potentials (see below). These results imply 390  
that an almost complete separation between the steric and the 391  
electronic effects in the context of few-electron reductions can 392  
indeed be achieved in this series of complexes. Changing the R 393  
group will strongly affect the energy of the LUMO while also 394  
having some impact on the steric properties at the carbon of 395  
the imino C=N bond, while changing the R<sub>1</sub> or R<sub>2</sub> groups 396  
should have considerable effects on the steric hindrance of the 397  
molecule (protecting the Mn and imino-N centers) but hardly 398  
affect its electronic properties. 399

The experimental and calculated carbonyl vibrational 400  
frequencies of the studied complexes are shown in Table 2. 401  
The calculated frequencies are in good agreement with the 402  
experimental values. Some systematic discrepancies are 403  
apparent: the high-energy A'(1) mode tends to be under- 404  
estimated by  $\sim 10$  cm<sup>-1</sup>, the A'' mode tends to have a lower 405  
deviation of only  $\sim 2$  cm<sup>-1</sup>, and the low-energy A'(2) mode 406  
tends to be overestimated by  $\sim 10$  cm<sup>-1</sup>. It is clear that 407  
attachment of the methyl group as R increases the electron 408  
density on the metal center and thus also the Mn to CO  $\pi$  409  
back-bonding, as evidenced by the smaller values of  $\nu(\text{CO})$  for 410

**Table 1. Frontier Orbitals of the Complexes 1–5 and the Corresponding Five-Coordinate Anions Calculated at the B3LYP/SDD+6-311G(d,p)/IEFPCM Level<sup>a</sup>**

HOMO	LUMO	HOMO	LUMO
Parent Complex		Five-coordinate anion	
MnIMP		MnIMP	
 $\epsilon = -6.31 \text{ eV}$	 $\epsilon = -2.84 \text{ eV}$	 $\epsilon = -3.67 \text{ eV}$	 $\epsilon = -1.18 \text{ eV}$
MnIPIMP		MnIPIMP	
 $\epsilon = -6.33 \text{ eV}$	 $\epsilon = -2.81 \text{ eV}$	 $\epsilon = -3.70 \text{ eV}$	 $\epsilon = -1.01 \text{ eV}$
MnDIPIMP		MnDIPIMP	
 $\epsilon = -6.31 \text{ eV}$	 $\epsilon = -2.83 \text{ eV}$	 $\epsilon = -3.67 \text{ eV}$	 $\epsilon = -0.99 \text{ eV}$
MnTBIMP		MnTBIMP	
 $\epsilon = -6.36 \text{ eV}$	 $\epsilon = -2.80 \text{ eV}$	 $\epsilon = -3.64 \text{ eV}$	 $\epsilon = -1.02 \text{ eV}$
MnTBIEP		MnTBIEP	
 $\epsilon = -6.31 \text{ eV}$	 $\epsilon = -2.81 \text{ eV}$	 $\epsilon = -3.67 \text{ eV}$	 $\epsilon = -1.01 \text{ eV}$

<sup>a</sup>Isovalue of 0.04 ( $e \text{ bohr}^{-3}$ )<sup>1/2</sup>.

MnTBIEP in comparison to the IMP subseries (complexes 1–4). However, substitution at R<sub>1</sub> and R<sub>2</sub> has only a slight effect on the frequencies. It should be noted that the magnitude of these effects is small ( $<10 \text{ cm}^{-1}$ ) and that it is beyond the scope of this computational work to unravel the various factors effecting changes in CO stretching frequencies.<sup>50</sup>

The results of DFT calculations (Table 2) of IR spectra for the parent Br complexes  $[\text{MnBr}(\text{CO})_3(\alpha\text{-diimine})]$  (1–5) and the corresponding  $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\alpha\text{-diimine})]^+$  (cationic

aquo complexes) match the experimental data well. We therefore use the calculated  $\nu(\text{CO})$  wavenumbers for the hydrolyzed aquo and reduced (dimer and anion) species to aid the analysis of the IR spectra and product assignment in the course of the corresponding cathodic IR-SEC experiments (vide infra).

Adding electron-donating groups (<sup>t</sup>Pr, <sup>t</sup>Bu) to the phenyl ring of the IMP subseries does not have a large effect on the  $\nu(\text{CO})$  frequency, the band positions being virtually unchanged

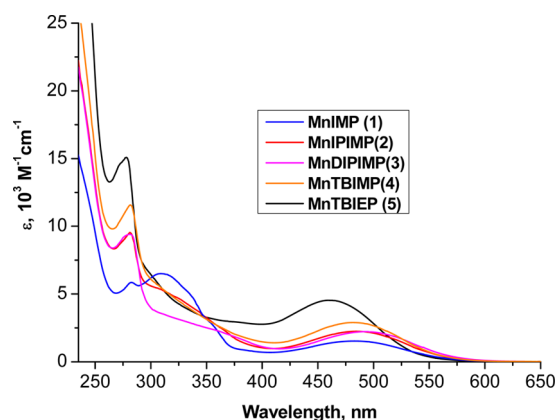


**Table 2.** Experimentally Obtained and Calculated Frequencies of Carbonyl Stretching Vibrations,  $\nu(\text{CO})$ , of the Mn Complexes in Their Neutral Form (1–5) and Transient One-Electron-Reduced Form, as well as Five-Coordinate Anion, a Cationic Aqua Complex, and an Mn–Mn Bound Dimer<sup>a</sup>

species	$\nu(\text{CO})/\text{cm}^{-1}$	
	calcd	exptl
[MnBr(CO) <sub>3</sub> (IMP)] (1)	2020, 1943, 1931	2029, 1941, 1926
[MnBr(CO) <sub>3</sub> (IMP)] <sup>−</sup>	1992, 1906, 1897	not obsd
[Mn(CO) <sub>3</sub> (H <sub>2</sub> O)(IMP)] <sup>+</sup>	2046, 1966, 1957	2051, 1964, 1958 <sup>b</sup>
[Mn(CO) <sub>3</sub> (IMP)] <sup>−</sup>	1906, 1830, 1813	1930, 1826
[Mn(CO) <sub>3</sub> (IMP)] <sub>2</sub>	1964, 1918, 1891, 1882, 1872, 1868	1994, 1949, 1902, 1875
[MnBr(CO) <sub>3</sub> (IPIMP)] (2)	2020, 1945, 1929	2029, 1943, 1923
[MnBr(CO) <sub>3</sub> (IPIMP)] <sup>−</sup>	1988, 1905, 1891	not obsd
[Mn(CO) <sub>3</sub> (H <sub>2</sub> O)(IPIMP)] <sup>+</sup>	2044, 1963, 1956	2049, 1959 (br)
[Mn(CO) <sub>3</sub> (IPIMP)] <sup>−</sup>	1905, 1826, 1808	1929, 1824
[Mn(CO) <sub>3</sub> (IPIMP)] <sub>2</sub>	1964, 1917, 1890, 1881, 1866, 1860	1981, 1949, 1901, 1882, 1862
[MnBr(CO) <sub>3</sub> (DIPIMP)] (3)	2019, 1945, 1929	2028, 1944, 1922
[MnBr(CO) <sub>3</sub> (DIPIMP)] <sup>−</sup>	1985, 1906, 1890	not obsd
[Mn(CO) <sub>3</sub> (H <sub>2</sub> O)(DIPIMP)] <sup>+</sup>	2045, 1964, 1957	2050, 1960 (br) <sup>b</sup>
[Mn(CO) <sub>3</sub> (DIPIMP)] <sup>−</sup>	1903, 1824, 1806	1929, 1829/1822
[Mn(CO) <sub>3</sub> (DIPIMP)] <sub>2</sub>	1965, 1918, 1890, 1880, 1860, 1850	not obsd
[MnBr(CO) <sub>3</sub> (TBIMP)] (4)	2020, 1947, 1925	2029, 1945, 1923
[MnBr(CO) <sub>3</sub> (TBIMP)] <sup>−</sup>	1988, 1907, 1890	not obsd
[Mn(CO) <sub>3</sub> (H <sub>2</sub> O)(TBIMP)] <sup>+</sup>	2045, 1965, 1956	not obsd
[Mn(CO) <sub>3</sub> (TBIMP)] <sup>−</sup>	1906, 1827, 1807	1928, 1823
[Mn(CO) <sub>3</sub> (TBIMP)] <sub>2</sub>	1964, 1916, 1889, 1879, 1862, 1854	not obsd
[MnBr(CO) <sub>3</sub> (TBIEP)] (5)	2018, 1944, 1921	2028, 1943, 1917
[MnBr(CO) <sub>3</sub> (TBIEP)] <sup>−</sup>	1980, 1904, 1883	not obsd
[Mn(CO) <sub>3</sub> (H <sub>2</sub> O)(TBIEP)] <sup>+</sup>	2042, 1962, 1950	2048, 1960, 1954
[Mn(CO) <sub>3</sub> (TBIEP)] <sup>−</sup>	1897, 1819, 1798	1922, 1814 (br)
[Mn(CO) <sub>3</sub> (TBIEP)] <sub>2</sub>	1958, 1909, 1880, 1870, 1850, 1841	not obsd

<sup>a</sup>In acetonitrile at 293 K. <sup>b</sup>Positions are approximate, as the parent CO stretching vibrations obscure those of the cationic aqua complex.

The UV–vis absorption spectra (Figure 2) are consistent with the nature of the frontier orbitals obtained from the



**Figure 2.** Electronic absorption spectra of the manganese complexes 1–5 studied in this work, in DCM at 293 K.

calculated data. The lowest energy absorption band for the complexes of the IMP subseries 1–4 occurs at approximately the same ca. 500 nm position. In contrast MnTBIEP (5) exhibits an absorption band with a maximum at a shorter wavelength, 460 nm, due to electron donation from the Me group which destabilizes the LUMO.

**Cyclic Voltammetry.** Electrochemical studies showed significant differences between the cathodic path of MnTBIEP (5) and those of the IMP subseries (1–4).

Under an N<sub>2</sub> atmosphere, [MnBr(CO)<sub>3</sub>(TBIEP)] shows a single reduction wave at  $E_{p,c} = -1.53$  V and an intense anodic wave at  $E_{p,a} = -1.3$  V observed on the reverse anodic scan. This behavior is similar to that of [MnBr(CO)<sub>3</sub>(<sup>i</sup>Pr-DAB)] (<sup>i</sup>Pr-DAB = 1,4-diisopropyl-1,4-diazabuta-1,3-diene),<sup>8</sup> which is reduced by an ECE mechanism. The initial one-electron reduction results in dissociation of the bromide to form a five-coordinate radical, [Mn(CO)<sub>3</sub>(TBIEP)]<sup>•</sup>, which is concomitantly reduced to the five-coordinate anion [Mn(CO)<sub>3</sub>(TBIEP)]<sup>−</sup> (reoxidized at  $-1.3$  V) at the potential required for the reduction of [MnBr(CO)<sub>3</sub>(TBIEP)]. A small anodic wave at  $-0.6$  V is characteristic of oxidation of [Mn(CO)<sub>3</sub>(TBIEP)]<sub>2</sub> formed in the course of the anodic path of the five-coordinate anion, and indicates that dimerization can still occur with R = CH<sub>3</sub>. The dimer could also be produced in a reaction of [Mn(CO)<sub>3</sub>(TBIEP)]<sup>−</sup> with neutral [MnBr(CO)<sub>3</sub>(TBIEP)] on the cathodic scan, but the absence of a cathodic wave for reduction of [Mn(CO)<sub>3</sub>(TBIEP)]<sub>2</sub> indicates that its reduction potential is too close to that of [MnBr(CO)<sub>3</sub>(TBIEP)] for a separate reduction wave to be observed.

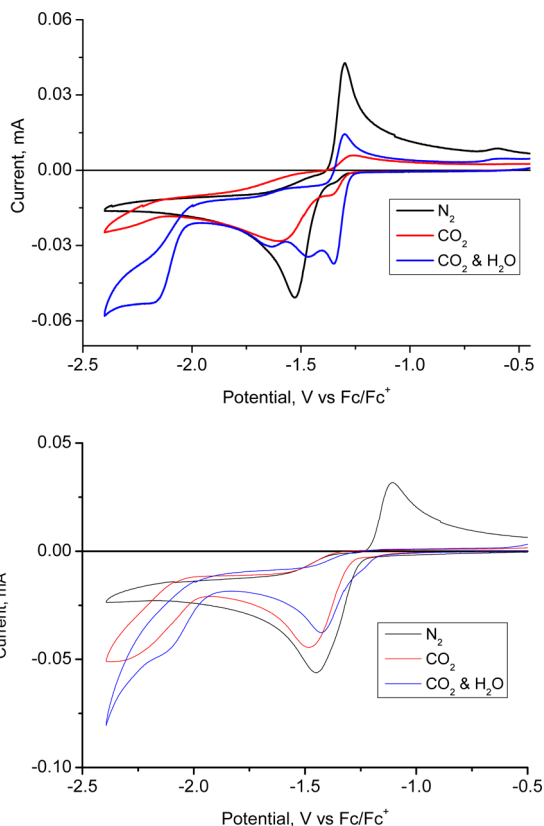
The CV traces of MnIMP obtained under a N<sub>2</sub> atmosphere show three cathodic reduction peaks at  $E_{p,c} = -1.28$ ,  $-1.41$ , and  $-1.54$  V and a strong anodic peak at  $E_{p,a} = -1.24$  V. The first reduction at  $-1.28$  V can be assigned to the cation [Mn(CO)<sub>3</sub>(H<sub>2</sub>O)(IMP)]<sup>+</sup>; it is likely that the peak at  $-1.41$  V is due to remaining nonhydrolyzed [MnBr(CO)<sub>3</sub>(IMP)] or a solvent adduct,<sup>11</sup> while the  $-1.54$  V wave corresponds to the reduction of the dimeric species (see also the IR spectroelectrochemical section below). The five-coordinate anion [Mn(CO)<sub>3</sub>(IMP)]<sup>−</sup> is probably the reduction product at all three different cathodic waves (the parent complex [MnBr(CO)<sub>3</sub>(IMP)], aquo complex, and the IMPMn–MnIMP

among complexes 1–4. The two higher-frequency bands are at 2028–2029 and 1943–1944 cm<sup>−1</sup> for all five complexes, while the lowest  $\nu(\text{CO})$  band is seen at 1923–1922 cm<sup>−1</sup> for the IMP series but is shifted to lower energy, 1917 cm<sup>−1</sup> in [MnBr(CO)<sub>3</sub>(TBIEP)], where the increased  $\pi$  back-donation is caused by R = Me. This invariability of  $\nu(\text{CO})$  frequencies, while the dihedral angles between the planes of the pyridine and phenyl moieties of the IP ligands are clearly changing drastically, from  $\sim 56$  to  $\sim 84^\circ$ , confirms the opportunity of the somewhat independent tuning of electronic and steric factors. Calculations performed on the five-coordinate anions of the studied compounds, [Mn(CO)<sub>3</sub>(diimine)]<sup>−</sup>, show trends very similar to what has been observed in the parent complexes. Both the HOMO and LUMO are predominantly delocalized over the tricarbonyl-Mn and  $\alpha$ -diimine metallacycle, with little participation from the phenyl ring, with the exception of MnIMP, the LUMO of which has a significant contribution from the phenyl moiety.



491 dimer), as evidenced by its anodic wave at  $E_{p,a} = -1.24$  V on  
 492 the reverse anodic scan (accompanied by the dimer oxidation  
 493 above  $-0.5$  V).

494 Over time a smaller cathodic wave emerges at  $E_{p,c} = -1.35$  V,  
 495 due to the aquo-coordinated cationic complex forming via  
 496 hydrolysis of the parent Br complex (see Figures S111 and S112  
 497 in the Supporting Information). Under an atmosphere of  $\text{CO}_2$   
 498 the anodic wave of  $[\text{Mn}(\text{CO})_3(\text{TBIEP})]^-$  at  $-1.3$  V disappears,  
 499 and the profile of the CV also changes (Figure 3), with a broad



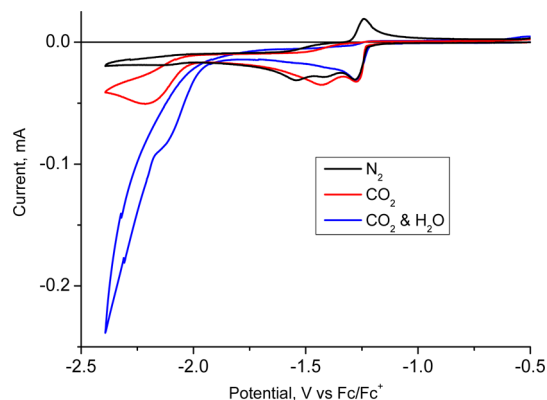
**Figure 3.** Cyclic voltammograms of 1 mM MnTBIEP (top panel) and MnTBIMP (bottom panel) in acetonitrile with 0.2 M  $[\text{Bu}_4\text{N}][\text{PF}_6]$  as supporting electrolyte, under a  $\text{N}_2$  atmosphere (black),  $\text{CO}_2$  atmosphere (red), and  $\text{CO}_2$  with 4.7% added water (blue) at a scan rate of  $0.1 \text{ V s}^{-1}$ .

500 cathodic wave of  $[\text{MnBr}(\text{CO})_3(\text{TBIEP})]$  shifted slightly  
 501 negatively, indicating an interaction with  $\text{CO}_2$ . However,  
 502 similar to the case for Mn-bpy complexes,<sup>2</sup> catalytic reduction  
 503 of  $\text{CO}_2$  in the absence of a Brønsted acid was not observed (the  
 504 small peak beginning around  $-2.18$  V is due to a small amount  
 505 of water entering the CV cell when it is being saturated with  
 506  $\text{CO}_2$ ). Addition of 0.3 mL of water leads to significant current  
 507 enhancement at  $-2.18$  V, in line with what has been observed  
 508 with  $[\text{MnBr}(\text{CO})_3(\text{iPr-DAB})]$ .<sup>8</sup>

509 Under a  $\text{CO}_2$  atmosphere, the increased cathodic current is  
 510 seen at  $\sim -2.2$  V for all complexes. We believe this is due to  
 511 some amount of the bicarbonate complex being formed, likely  
 512 due to traces of water in the  $\text{CO}_2$  used.<sup>33</sup> When 10% water is  
 513 added to the  $\text{CO}_2$ -saturated solution, a strong current  
 514 enhancement is observed at  $-2.21$  V. Importantly, CVs  
 515 recorded under a  $\text{N}_2$  atmosphere in acetonitrile in the presence  
 516 of water do not show catalytic current enhancement (see  
 517 Figures S114–S118 in the Supporting Information); thus, both

$\text{CO}_2$  and water are required for the current enhancement to be  
 518 observed. 519

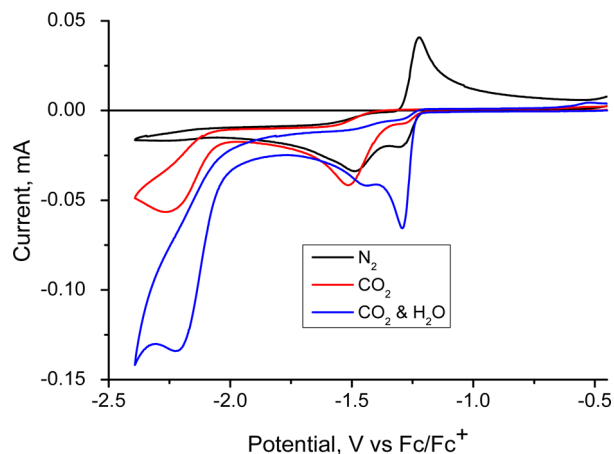
Under a  $\text{CO}_2$  atmosphere, no anodic wave corresponding to  
 520 reoxidation of the five-coordinate anion is observed for the least  
 521 sterically hindered  $[\text{Mn}(\text{CO})_3(\text{IMP})]^-$  (Figure 4) or for the  
 522 523



**Figure 4.** Cyclic voltammograms of 1 mM MnIMP in acetonitrile with 0.2 M  $[\text{Bu}_4\text{N}][\text{PF}_6]$  at a scan rate of  $0.1 \text{ V s}^{-1}$ , under an atmosphere of  $\text{N}_2$  (black),  $\text{CO}_2$  (red), and  $\text{CO}_2$  with 4.7%  $\text{H}_2\text{O}$  (blue).

monosubstituted complexes **2** and **4**, a behavior indicative of a  
 523 rapid reaction of the anion with  $\text{CO}_2$ . A diminished but clear  
 524 anodic wave of  $[\text{Mn}(\text{CO})_3(\text{TBIEP})]^-$  can be observed under a  
 525  $\text{CO}_2$  vs a  $\text{N}_2$  atmosphere (Figure 3), suggesting that  
 526  $[\text{Mn}(\text{CO})_3(\text{TBIEP})]^-$  associates with  $\text{CO}_2$  less efficiently.  
 527 While, similarly to MnIPIMP, no anodic wave corresponding  
 528 to  $[\text{Mn}(\text{CO})_3(\text{TBIMP})]^-$  reoxidation under a  $\text{CO}_2$  atmosphere  
 529 could be observed, indicating that  $\text{CO}_2$  association is rapid, the  
 530 overall current enhancement for this complex is comparatively  
 531 low, indicating lower efficiency at reducing  $\text{CO}_2$ , perhaps due to  
 532 the bicarbonate intermediate somewhat preventing the recovery  
 533 of the five-coordinate catalytic species. 534

Under  $\text{N}_2$ , reduction of  $[\text{MnBr}(\text{CO})_3(\text{IPIMP})]$  is seen at  $E_{p,c}$   
 535  $-1.49$  V, accompanied by a wave at  $E_{p,c} = -1.29$  V, assigned to  
 536 the cationic aqua complex  $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{IPIMP})]^+$  (Figure  
 537 5). As discussed above, upon addition of  $\text{CO}_2$  the oxidation  
 538 539 wave of the anion  $[\text{Mn}(\text{CO})_3(\text{IPIMP})]^-$  is not observed,  
 540 indicating a rapid reaction between the five-coordinate anion



**Figure 5.** Cyclic voltammograms of 1 mM MnIPIMP in acetonitrile with 0.2 M  $[\text{Bu}_4\text{N}][\text{PF}_6]$  at a scan rate of  $0.1 \text{ V s}^{-1}$ , under an atmosphere of  $\text{N}_2$  (black),  $\text{CO}_2$  (red), and  $\text{CO}_2$  with 4.7%  $\text{H}_2\text{O}$  (blue).

541 and CO<sub>2</sub>. Some current enhancement at -2.26 V is observed  
 542 upon saturation with CO<sub>2</sub>, which is enhanced greatly upon the  
 543 addition of 0.3 mL of water (the current enhancement  
 544 corresponds to the cathodic wave of the bicarbonate complex,  
 545 identified in the IR spectra (vide infra): some catalysis occurs  
 546 due to hydrolysis caused for example by residual water in the  
 547 electrolyte or in the CO<sub>2</sub>).

548 CV of MnTBIMP (Figure 3, bottom panel) is similar to that  
 549 of MnIPIMP and MnTBIEP with a strong cathodic wave at  
 550 -1.45 V. At ca. -2.28 V current enhancements ascribed to CO<sub>2</sub>  
 551 reduction can be observed under CO<sub>2</sub> and CO<sub>2</sub> with added  
 552 H<sub>2</sub>O, though the *i*<sub>cat</sub>/*i*<sub>p</sub> values (Table S11 in the Supporting  
 553 Information) are somewhat lower in comparison to the other  
 554 complexes studied here. Importantly, the anodic wave of the  
 555 five-coordinate anion reoxidation is not detected for MnIPIMP  
 556 and MnTBIMP but is clearly seen for slower reacting  
 557 MnTBIEP and MnDIPIMP anions.

558 MnDIPIMP shows significant differences in the CV traces in  
 559 comparison to the other complexes of the IMP subseries  
 560 (Figure 6). Similarly to the IMP and IPIMP complexes, a

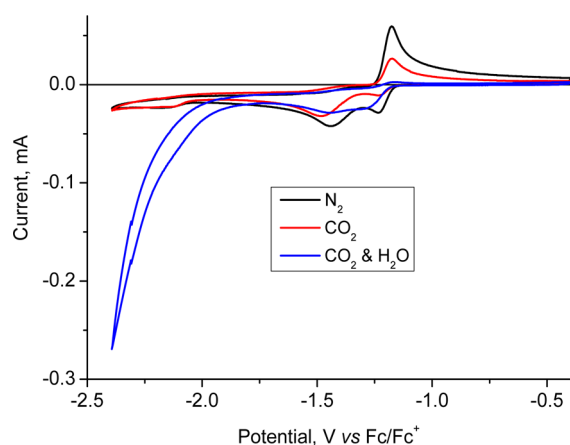


Figure 6. Cyclic voltammograms of 1 mM MnDIPIMP in acetonitrile with 0.2 M [Bu<sub>4</sub>N][PF<sub>6</sub>] at a scan rate of 0.1 V s<sup>-1</sup>, under an atmosphere of N<sub>2</sub> (black), CO<sub>2</sub> (red), and CO<sub>2</sub> with 4.7% H<sub>2</sub>O (blue).

561 formation of an aqua cation complex ([Mn(CO)<sub>3</sub>(H<sub>2</sub>O)-  
 562 (DIPIMP)]<sup>+</sup>) is observed in solution. However, upon  
 563 saturation with CO<sub>2</sub> no additional processes (intermediate  
 564 bicarbonate complex reduction) or current enhancement below  
 565 -2 V is observed and the anodic peak due to oxidation of  
 566 [Mn(CO)<sub>3</sub>(DIPIMP)]<sup>-</sup> does not fully disappear. This suggests  
 567 that the reduced complex is less prone to interact with CO<sub>2</sub>, as  
 568 would be expected due to the increased steric hindrance and  
 569 structural rigidity of the complex arising from the two <sup>i</sup>Pr  
 570 substituents at the N-phenyl rings.

571 **IR and UV-Vis Spectroelectrochemistry under an  
 572 Inert Atmosphere.** IR spectroscopy<sup>20</sup> is an ideal tool to  
 573 monitor the cathodic processes in the studied complexes, due  
 574 to presence of the carbonyl ligands as strong IR reporters.  
 575 Table 2 gives the key experimental and calculated vibrational  
 576 frequencies for the starting complexes and several relevant  
 577 intermediate and dimer species. IR spectroelectrochemistry  
 578 (IR-SEC) was used to probe the intermediates produced upon  
 579 reduction and to monitor their presence during CO<sub>2</sub> reduction.  
 580 IR spectra of MnTBIEP (Figure 7) show, upon the first  
 581 reduction, depletion of the parent  $\nu(\text{CO})$  bands, with new  
 582 bands growing in at 1922 and 1898 cm<sup>-1</sup> and a broad feature at

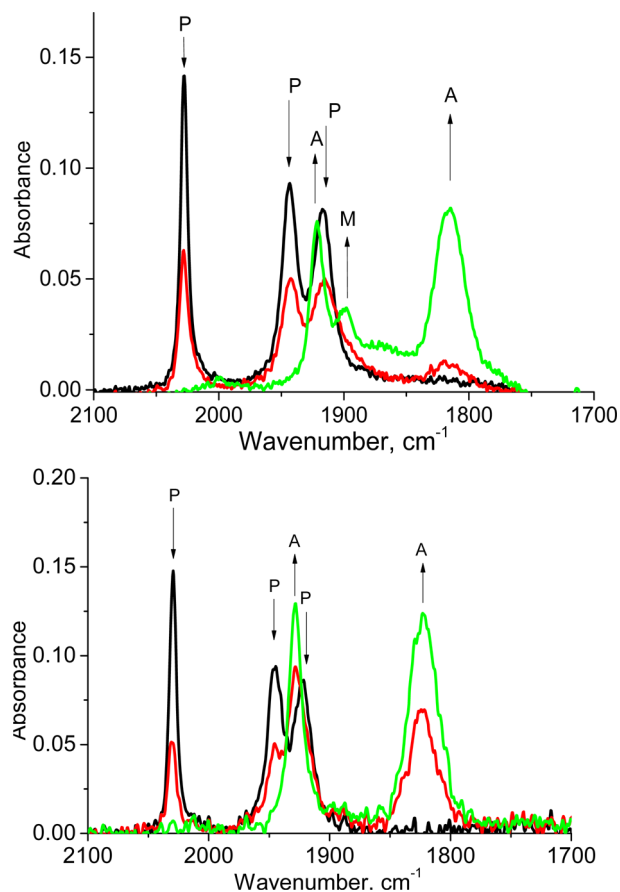
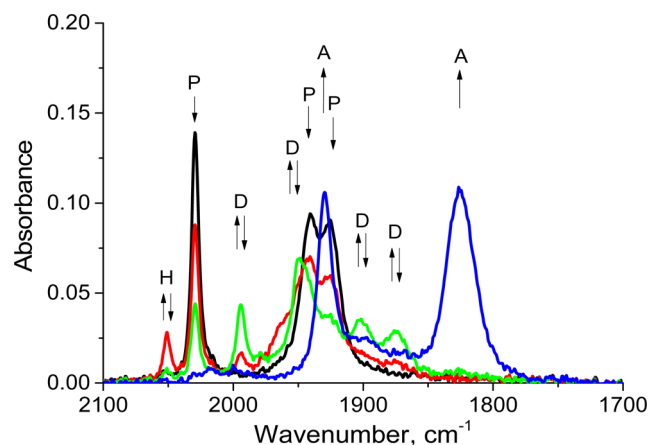


Figure 7. IR spectral changes accompanying in situ reduction of complexes in Ar-saturated acetonitrile/0.2 M [Bu<sub>4</sub>N][PF<sub>6</sub>] within an OTTE cell. (top) For MnTBIEP, a direct reduction of the parent complex (black line) to the five-coordinate anion (green line) is observed. (P) [MnBr(CO)<sub>3</sub>(TBIEP)]; (A) [Mn(CO)<sub>3</sub>(TBIEP)]<sup>-</sup>; (M) an unassigned side product. (bottom) For MnTBIMP, a direct reduction of the parent complex (black line) to the five-coordinate anion (green line) is observed: (P) [MnBr(CO)<sub>3</sub>(TBIMP)]; (A) [Mn(CO)<sub>3</sub>(TBIMP)]<sup>-</sup>.

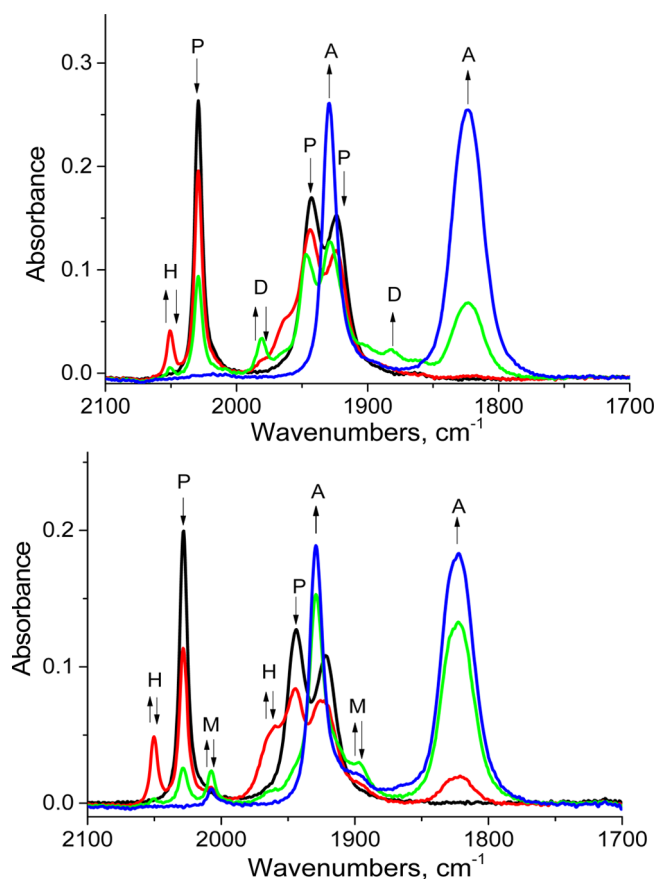
1814 cm<sup>-1</sup>. The bands at 1922 and 1814 cm<sup>-1</sup> can be assigned  
 583 to the five-coordinate anion [Mn(CO)<sub>3</sub>(TBIEP)]<sup>-</sup>, an assign-  
 584 ment supported by DFT calculations. The band at 1898 cm<sup>-1</sup>,  
 585 which grows in after the five-coordinate anion begins to form,  
 586 could tentatively be attributed to a decomposition product.  
 587 UV-vis spectroelectrochemistry (Figure S113 in the Support-  
 588 ing Information) supports this notion, as only a band at ca. 570  
 589 nm has been detected, which corresponds to the five-  
 590 coordinate anion. Differently from the MnIMP and MnIPIMP  
 591 complexes (see below), there is no indication of dimer  
 592 ([Mn(CO)<sub>3</sub>(TBIEP)]<sub>2</sub>) formation during the reduction of  
 593 MnTBIEP on the time scale of the experiments performed.  
 594

MnTBIMP mirrors the behavior of MnTBIEP with the bands  
 595 at 2029, 1945, and 1923 cm<sup>-1</sup> corresponding to the parent  
 596 complex being replaced concertedly with bands at 1928 and  
 597 1823 cm<sup>-1</sup> corresponding to the five-coordinate anion, with no  
 598 intermediate species being observed. This would suggest that  
 599 the direct formation of the five-coordinate anion is due to the  
 600 steric demands of the <sup>t</sup>Bu group, since the mono-<sup>i</sup>Pr derivative  
 601 2 does exhibit dimer formation (Table 1).  
 602

The results of the IR-SEC study of MnIMP are shown in  
 603 Figure 8. The first reduction of MnIMP in CH<sub>3</sub>CN under an Ar  
 604 atmosphere is accompanied by depletion of the parent IR bands  
 605



**Figure 8.** IR spectral changes accompanying in situ reduction of MnIMP in Ar-saturated acetonitrile/0.2 M  $[\text{Bu}_4\text{N}][\text{PF}_6]$  within an OTTLE cell. The parent complex  $[\text{MnBr}(\text{CO})_3(\text{IMP})]$  (P, black line), and aquo cation  $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{IMP})]^+$  (H, additional features in the red spectrum) are reduced to the dimer  $[\text{MnBr}(\text{CO})_3(\text{IMP})]_2$  (D, green line) followed by reduction of the dimer to the five-coordinate anion  $[\text{Mn}(\text{CO})_3(\text{IMP})]^-$  (A, blue line). The intermediate spectrum (red line) recorded between those of the parent complex and the dimer also shows the features of the aquo complex.



**Figure 9.** IR spectral changes accompanying in situ reduction of the complexes in Ar-saturated acetonitrile/0.2 M  $[\text{Bu}_4\text{N}][\text{PF}_6]$  within an OTTLE cell. (top) MnIPIMP, with concurrent formation of a dimer and a five-coordinate anion on reduction of the parent complex being observed: (P)  $[\text{MnBr}(\text{CO})_3(\text{IPIMP})]$ ; (D)  $[\text{Mn}(\text{CO})_3(\text{IPIMP})]_2$ ; (A)  $[\text{Mn}(\text{CO})_3(\text{IPIMP})]^-$ ; (H)  $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{IPIMP})]^+$ . (bottom) MnDIPIMP, with reduction of the parent complex to a five-coordinate anion being observed: (P)  $[\text{MnBr}(\text{CO})_3(\text{DIPIMP})]$ ; (A)  $[\text{Mn}(\text{CO})_3(\text{DIPIMP})]^-$ ; (H)  $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DIPIMP})]^+$ ; (M)  $[\text{Mn}(\text{CO})_3(\text{MeCN})(\text{DIPIMP})]^*$ .

606 at 2029, 1941, and 1926  $\text{cm}^{-1}$ . Simultaneously, the growth of  
 607 new bands at 1994, 1949, 1902, and 1875  $\text{cm}^{-1}$  is seen, which  
 608 are characteristic of the Mn–Mn dimer<sup>8,9,13,30</sup>  $[\text{Mn}-$   
 609  $(\text{CO})_3(\text{IMP})]_2$ . Additionally, a peak at 2051  $\text{cm}^{-1}$  grows in  
 610 initially, which is assigned to the intermediate aqua cation  
 611  $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{IMP})]^+$  observed also by cyclic voltammetry.  
 612 Further reduction of the dimer leads to formation of broad  
 613 absorption bands at 1826 and 1930  $\text{cm}^{-1}$ , once the formation of  
 614 the dimer species is complete. These features are characteristic  
 615 of the formation of the five-coordinate anion<sup>8,9,13</sup>  $[\text{Mn}-$   
 616  $(\text{CO})_3(\text{IMP})]^-$ . UV–vis spectroelectrochemistry performed  
 617 in parallel with the IR–SEC experiment confirms the presence  
 618 of both of these species (Figure S114 in the Supporting  
 619 Information) via the broad absorption band at ca. 800 nm  
 620 (assigned to the dimer) and the intense absorption at ca. 675  
 621 nm (assigned to the five-coordinate anion).<sup>8</sup> All complexes in  
 622 the IMP subseries exhibited a small transient peak at ca. 2050  
 623  $\text{cm}^{-1}$  upon reduction. This is assigned to the aquo complex  
 624  $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{IMP})]^+$ .

625 Differently from MnIMP, MnIPIMP showed concurrent  
 626 formation of the dimer and the five-coordinate anion upon  
 627 reduction of the parent complex (Figure 9, top). The  
 628 introduction of the isopropyl substituent at the phenyl ring  
 629 leads to the observation of a small amount of the five-  
 630 coordinate anion  $[\text{Mn}(\text{CO})_3(\text{IPIMP})]^-$  (absorbing at 1929 and  
 631 1824  $\text{cm}^{-1}$ ), which grows in alongside peaks indicative of dimer  
 632 formation (1981, 1949, 1901, 1882, and 1862  $\text{cm}^{-1}$ ).

633 Importantly, the IR absorption bands, corresponding to both  
 634 the dimer and the five-coordinate anion, grew in simulta-  
 635 neously. UV–vis spectroelectrochemistry confirmed the  
 636 presence of both dimer and five-coordinate species in this  
 637 case, as is evident from Figure S113 in the Supporting  
 638 Information).

639 In contrast, only the five-coordinate anion is detected already  
 640 from the onset of the reduction of MnDIPIMP under the  
 641 experimental conditions used. In this case, there is no evidence  
 642 for the dimer formation during the reduction of the parent  
 643 complex. As shown in Figure 9 (bottom), an intense peak at

1823  $\text{cm}^{-1}$ , assigned to the five-coordinate anion, grew in,  
 followed closely by smaller peaks at 2007 and 1899  $\text{cm}^{-1}$ . The  
 second peak assigned to the five-coordinate anion at 1929  $\text{cm}^{-1}$   
 was masked by the absorption of the parent complex at the  
 beginning of the reduction process. We tentatively assign the  
 peaks at 2007/1899  $\text{cm}^{-1}$  to the solvent-coordinated radical  
 species  $[\text{Mn}(\text{CO})_3(\text{MeCN})(\text{DIPIMP})]^*$ , in analogy with  
 $[\text{Re}(\text{CO})_3(\text{PrCN})(^i\text{Pr-PyCa})]^{17}$  ( $^i\text{Pr-PyCa}$  = (isopropylimino)-  
 pyridine; PrCN = butyronitrile) which shows  $\nu(\text{CO})$  bands at  
 2005 and 1885 (br)  $\text{cm}^{-1}$ . Further, since the anodic wave of the  
 dimer oxidation is not observed in the CV of MnDIPIMP, but a  
 reduced radical species is observed in IR–SEC, it is evident  
 that the DIPIMP ligand prevents dimerization.

MnTBIMP shows behavior intermediate to that of  
 MnTBIEP and MnIPIMP: similarly to MnTBIEP, the  $^i\text{Bu}$   
 substituent prevent dimer formation upon reduction. However,  
 differently from MnTBIEP, and similar to MnIPIMP, a rapid  
 reaction with  $\text{CO}_2$  takes place, which in the case of MnTBIEP is  
 considerably slowed by the R = Me group. It is important to  
 note that if Mn–Mn dimer is reduced at the same or even less  
 negative potentials than that of the parent complex, it will not  
 be detected in the studies.<sup>9</sup> Thus, the comments above



666 regarding the absence of dimer formation only relate to the Br  
 667 complexes studied here. Substituting Br<sup>-</sup> with a different group,  
 668 which would lead to the parent complex being reduced at less  
 669 negative potentials, may permit detection of these species. Five-  
 670 coordinate complex formation appears to correlate with a less  
 671 negative first reduction potential (see Table 3). A comparable

**Table 3. Cathodic Potentials (V, vs Fc/Fc<sup>+</sup>) of the Parent Complexes [MnBr(CO)<sub>3</sub>(IP)] (1 mM, Acetonitrile, 0.2 M [Bu<sub>4</sub>N][PF<sub>6</sub>]) and Corresponding Cationic Mn Aquo Derivatives Formed in Situ by Partial Hydrolysis**

complex	<i>E</i> <sub>p,c</sub>	catalytic potential <sup>b</sup>
[MnBr(CO) <sub>3</sub> (IMP)] (1)	-1.41, -1.54 <sup>a</sup>	-2.21
[Mn(CO) <sub>3</sub> (H <sub>2</sub> O)(IMP)] <sup>+</sup>	-1.28	
[MnBr(CO) <sub>3</sub> (IPIMP)] (2)	-1.49	-2.26
[Mn(CO) <sub>3</sub> (H <sub>2</sub> O)(IPIMP)] <sup>+</sup>	-1.29	
[MnBr(CO) <sub>3</sub> (DIPIMP)] (3)	-1.44	-2.16
[Mn(CO) <sub>3</sub> (H <sub>2</sub> O)(DIPIMP)] <sup>+</sup>	-1.23	
[MnBr(CO) <sub>3</sub> (TBIMP)] (4)	-1.45	~-2.28
[MnBr(CO) <sub>3</sub> (TBIEP)] (5)	-1.53	-2.18
[Mn(CO) <sub>3</sub> (H <sub>2</sub> O)(TBIEP)] <sup>+</sup>	-1.35	

<sup>a</sup>This process probably corresponds to a reduction of the dimer.

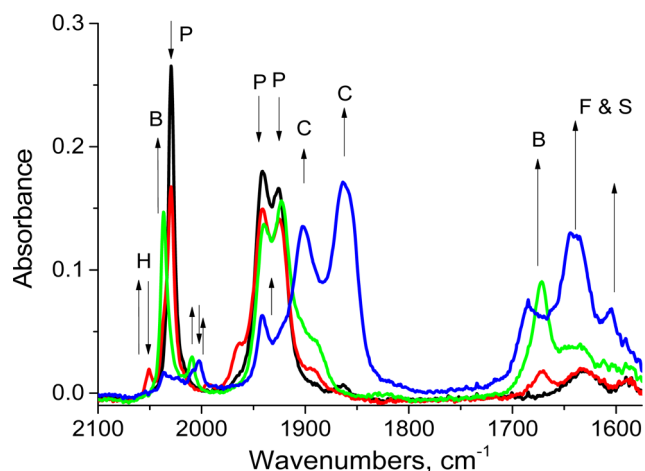
<sup>b</sup>Largely coinciding with the reduction of a bicarbonate complex (see the spectroelectrochemical section).

672 correlation was found for Mn-R-DAB complexes and sterically  
 673 hindered 2,2'-bipyridines already reported in the literature.  
 674 These complexes also exhibit less negative first reduction  
 675 potentials in comparison to their less sterically hindered  
 676 counterparts and form five-coordinate anions directly upon  
 677 reduction.<sup>8,25</sup>

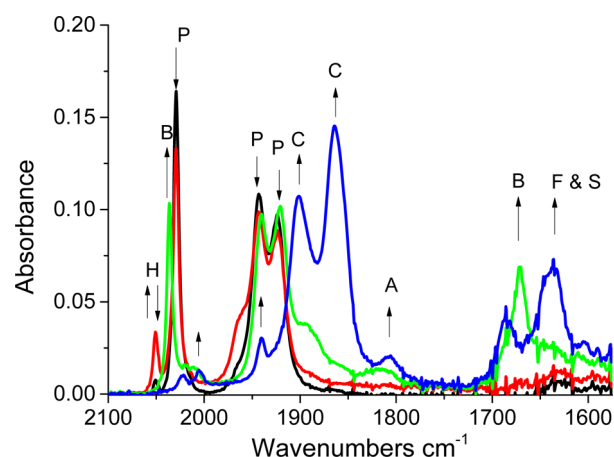
678 **IR and UV-Vis Spectroelectrochemistry under a CO<sub>2</sub>**  
 679 **Atmosphere.** Electrochemical behavior under a CO<sub>2</sub> atmo-  
 680 sphere is vastly different from that under a N<sub>2</sub> or Ar atmosphere.  
 681 The electrocatalytic reduction of CO<sub>2</sub> with the four Mn  
 682 complexes can be described in terms of three different types of  
 683 behavior, largely controlled by the steric hindrance of the active  
 684 imino C=N bond. MnIMP and MnIPIMP are relatively  
 685 unhindered, and the catalytic behaviors are almost identical.  
 686 The initial reduction of parent and/or the cationic aqua  
 687 complex results in the formation of the two-electron-reduced  
 688 five-coordinate anion that reacts efficiently with CO<sub>2</sub>; no dimer  
 689 is observed during the reduction of MnIMP (Figure 10) or  
 690 MnIPIMP (Figure 11).

691 The catalytic process at the initial cathodic wave is, however,  
 692 inhibited by the rapid formation of a stable bicarbonate  
 693 complex, absorbing at 2036, 1940, 1924, and 1671 cm<sup>-1</sup> for the  
 694 IPIMP species, in line with the reports for sterically hindered  
 695 Mn-mesityl-bipyridine<sup>25</sup> complexes and Mn-R-DAB com-  
 696 plexes.<sup>8</sup> A further negative potential shift of ca. 0.7 V is needed  
 697 to reduce the bicarbonate complex, resulting in the recovery of  
 698 the five-coordinate anion that triggers the catalytic conversion  
 699 of CO<sub>2</sub>.

700 For the nonhindered IMP and IPIMP ligands the five-  
 701 coordinate anion reacts rapidly and is not observed in the IR  
 702 spectra on this time scale (for IMP) and only at a low  
 703 concentration (for IPIMP). The production of CO in the thin  
 704 solution layer results in the displacement of the α-diimine  
 705 ligand in the five-coordinate anion, forming the pentacarbonyl  
 706 species [Mn(CO)<sub>5</sub>]<sup>-</sup> clearly seen in the IR spectra via the  
 707 growth of bands at 1897 and 1865 cm<sup>-1</sup> (species C in Figures  
 708 10–13). Remarkably, in these two cases only a comparatively



**Figure 10.** IR spectral changes accompanying in situ reduction of MnIMP ([MnBr(CO)<sub>3</sub>(IMP)]) in CO<sub>2</sub>-saturated acetonitrile/0.2 M [Bu<sub>4</sub>N][PF<sub>6</sub>] within an OTTLE cell: (P) [MnBr(CO)<sub>3</sub>(IMP)]; (B) [Mn(CO)<sub>3</sub>(IMP)(η<sup>1</sup>-OCO<sub>2</sub>H)]<sup>-</sup>; (C) [Mn(CO)<sub>5</sub>]<sup>-</sup>; (H) [Mn(CO)<sub>3</sub>(H<sub>2</sub>O)(IMP)]<sup>+</sup>; (F and S) free bicarbonate (OCO<sub>2</sub>H<sup>-</sup>) and subordinate formate (OCHO<sup>-</sup>) accompanying the catalytic reduction of CO<sub>2</sub> to CO.

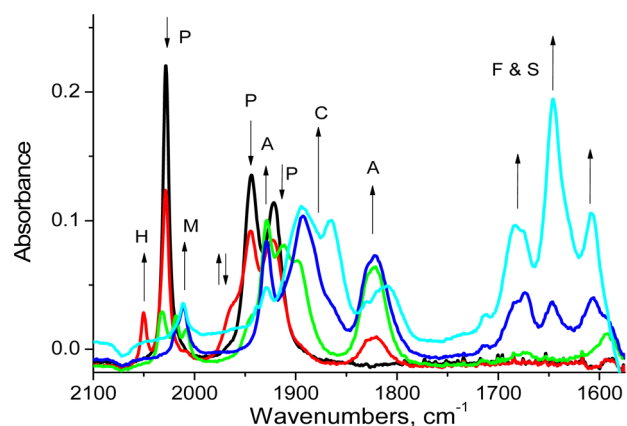


**Figure 11.** IR spectral changes accompanying in situ reduction of MnIPIMP ([MnBr(CO)<sub>3</sub>(IPIMP)]) in CO<sub>2</sub>-saturated acetonitrile/0.2 M [Bu<sub>4</sub>N][PF<sub>6</sub>] in an OTTLE cell: (P) [MnBr(CO)<sub>3</sub>(IPIMP)]; (A) [Mn(CO)<sub>3</sub>(IPIMP)]<sup>-</sup>; (B) [Mn(CO)<sub>3</sub>(IPIMP)(η<sup>1</sup>-OCO<sub>2</sub>H)]<sup>-</sup>; (C) [Mn(CO)<sub>5</sub>]<sup>-</sup>; (H) [Mn(CO)<sub>3</sub>(H<sub>2</sub>O)(IPIMP)]<sup>+</sup>; (F and S) free bicarbonate (OCO<sub>2</sub>H<sup>-</sup>) and subordinate formate (OCHO<sup>-</sup>) accompanying the catalytic reduction of CO<sub>2</sub> to CO.

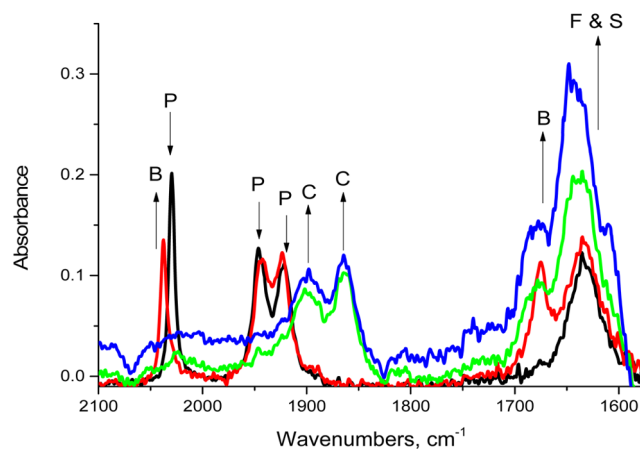
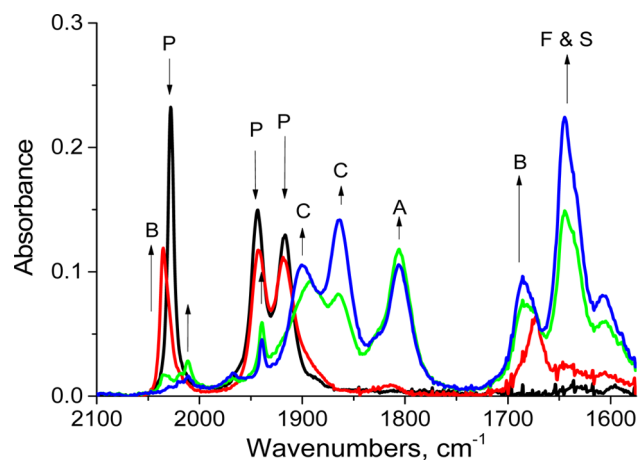
small amount of free bicarbonate or free formate (1685, 1638, 709  
 and 1604 cm<sup>-1</sup> for the IPIMP species) relative to [Mn(CO)<sub>5</sub>]<sup>-</sup> 710  
 is observed, marking the high catalytic efficiency toward CO 711  
 production. 712

Upon reduction of the more C=N hindered DIPIMP 713  
 complex, the five-coordinate anion formed does not react with 714  
 CO<sub>2</sub> efficiently and a metastable population of the anionic five- 715  
 coordinate MnDIPIMP species [Mn(CO)<sub>3</sub>(DIPIMP)]<sup>-</sup> is 716  
 detected even under a high excess of CO<sub>2</sub>. Interestingly, and 717  
 differently from the other complexes in the Mn-IP series, the 718  
 formation of a bicarbonate complex is only detected at the 719  
 potential corresponding to the reduction of CO<sub>2</sub>-associated 720  
 species at around -2 V vs Fc/Fc<sup>+</sup>, while on prior coordination 721  
 of CO<sub>2</sub> to the five-coordinate anion at the parent MnDIPIMP 722  
 cathodic wave no bicarbonate ligand signature is detected. At 723  
 the catalytic potential where the bicarbonate complex is 724





**Figure 12.** IR spectral changes accompanying in situ reduction of MnDIPIMP in CO<sub>2</sub>-saturated acetonitrile/0.2 M [Bu<sub>4</sub>N][PF<sub>6</sub>] within an OTTLE cell: (P) [MnBr(CO)<sub>3</sub>(DIPIMP)]; (A) [Mn(CO)<sub>3</sub>(DIPIMP)]<sup>-</sup>; (B) [Mn(CO)<sub>3</sub>(DIPIMP)(η<sup>1</sup>-OCO<sub>2</sub>H)]; (H) aqua complex [Mn(CO)<sub>3</sub>(H<sub>2</sub>O)(DIPIMP)]<sup>+</sup>; (C) [Mn(CO)<sub>5</sub>]<sup>-</sup>; (M) [Mn(CO)<sub>3</sub>(MeCN)(DIPIMP)]<sup>+</sup>; (F and S) free bicarbonate (OCO<sub>2</sub>H<sup>-</sup>) and subordinate formate (OCHO<sup>-</sup>).



**Figure 13.** IR spectral changes accompanying in situ reduction of complexes in CO<sub>2</sub>-saturated acetonitrile/0.2 M [Bu<sub>4</sub>N][PF<sub>6</sub>] within an OTTLE cell. (top) For MnTBIEP: (P) [MnBr(CO)<sub>3</sub>(TBIEP)]; (A) [Mn(CO)<sub>3</sub>(TBIEP)]<sup>-</sup>; (B) [Mn(CO)<sub>3</sub>(TBIEP)(η<sup>1</sup>-OCO<sub>2</sub>H)]; (C) [Mn(CO)<sub>5</sub>]<sup>-</sup>; (F and S) free bicarbonate (OCO<sub>2</sub>H<sup>-</sup>) and formate (OCHO<sup>-</sup>) accompanying the catalytic reduction of CO<sub>2</sub> to CO. (bottom) For MnTBIMP: (P) [MnBr(CO)<sub>3</sub>(TBIMP)]; (B) [Mn(CO)<sub>3</sub>(TBIMP)(η<sup>1</sup>-OCO<sub>2</sub>H)]; (C) [Mn(CO)<sub>5</sub>]<sup>-</sup>; (F and S) free bicarbonate (OCO<sub>2</sub>H<sup>-</sup>) and formate (OCHO<sup>-</sup>) accompanying the catalytic reduction of CO<sub>2</sub> to CO.

725 reduced, the conversion of CO<sub>2</sub> to CO is also inefficient. A high  
726 concentration of the five-coordinate anion is still seen,  
727 converting slowly to [Mn(CO)<sub>5</sub>]<sup>-</sup> when the concentration of  
728 CO increases; at the same time the production of free  
729 bicarbonate (and free formate) is much higher in comparison  
730 to the MnIMP and MnIPIMP cases, marking the low catalytic  
731 efficiency toward CO production. Notably, the lower CO-  
732 stretching band of [Mn(CO)<sub>3</sub>(DIPIMP)]<sup>-</sup> becomes shifted  
733 from its standard position (1829/1822 cm<sup>-1</sup>) to lower energy  
734 (ca. 1810 cm<sup>-1</sup>) at the advanced stage of the catalytic  
735 conversion. This shift may indicate the presence of an  
736 observable adduct of the five-coordinate anion, most likely  
737 with CO<sub>2</sub> or formate (over the Mn–N=C bond). In this  
738 context it is interesting to note that the related Re-IP complex<sup>37</sup>  
739 forms the carbonate complex in two 1e-reduction steps, via a  
740 direct coordination to the Re center, without C=N being  
741 directly involved.

742 In the case of MnTBIEP the imino C=N bond is hindered  
743 both at the carbon atom via the methyl group and by the *tert*-  
744 butyl group on the phenyl moiety. There are similarities with  
745 but also differences from the hindered DIPIMP complex, which  
746 does not have a hindering group at the C atom of the imino  
747 C=N moiety. Upon reduction of the parent complex in CO<sub>2</sub>-  
748 saturated acetonitrile the five-coordinate anion [Mn-  
749 (CO)<sub>3</sub>(TBIEP)]<sup>-</sup> coordinates CO<sub>2</sub>, forming the bicarbonate  
750 complex readily (similar to IMP and IPIMP) with the  
751 characteristic IR absorption band at 1673 cm<sup>-1</sup>.<sup>8,30</sup>

752 A small amount of the five-coordinate anion [Mn-  
753 (CO)<sub>3</sub>(TBIEP)]<sup>-</sup> is observed in the initial step. Lowering the  
754 potential to around -1.5 V vs Fc/Fc<sup>+</sup> results in catalytic  
755 conversion of the bicarbonate complex; however, similar to  
756 MnDIPIMP this conversion is not efficient in comparison with  
757 MnIMP and MnIPIMP. This is shown via the slower growth of  
758 [Mn(CO)<sub>5</sub>]<sup>-</sup> in comparison to IPIMP and the greater  
759 quantities of free bicarbonate produced. As with MnDIPIMP  
760 the five-coordinate anion “adduct” form is observed with the  
761 lower energy CO-stretching band shifted to a lower wave-  
762 number (from 1814 to 1803 cm<sup>-1</sup>). Thus, hindering the imine  
763 C atom does not affect adduct formation between CO<sub>2</sub> and  
764 [Mn(CO)<sub>3</sub>(TBIEP)]<sup>-</sup>.

765 However, at the negative potentials where the bicarbonate  
766 complex is reduced (recovering the catalytic five-coordinate  
767 anion) the hindrance provided by the methyl and *tert*-butyl  
768 groups also negatively affects the catalytic formation of CO<sub>2</sub> to  
769 CO (as evidenced by large amounts of free bicarbonate and  
770 slow formation of [Mn(CO)<sub>5</sub>]<sup>-</sup> at lower CO concentration). It  
771 is not very clear whether this greater hindrance is due directly  
772 to the presence of the methyl group on the C position or  
773 whether this is due to the *tert*-butyl group inhibiting rotation  
774 of the phenyl moiety and preventing the five-coordinate anion  
775 from adopting a more suitable (pyramidal) geometry for CO<sub>2</sub>  
776 association.

777 Again, MnTBIMP behaves in a fashion similar to that of  
778 MnTBIEP. Upon reduction the parent complex rapidly  
779 associates CO<sub>2</sub>, forming the bicarbonate complex; as the  
780 reduction potential is lowered further, the bicarbonate complex  
781 is reduced, forming CO which is able to displace the TBIMP  
782 and forming [Mn(CO)<sub>5</sub>]<sup>-</sup>. One important difference is that  
783 significantly less (if any) five-coordinate anion is observed in  
784 the presence of CO<sub>2</sub> than was the case with both MnTBIEP

785 and MnDIPIMP. This suggests that <sup>t</sup>Bu is not as sterically  
786 demanding as two <sup>i</sup>Pr groups in these systems, as CO<sub>2</sub> is still  
787 able to coordinate.

788 **Estimation of Electrocatalytic Activity toward CO**  
789 **Production using Gas Chromatography.** The CO  
790 concentration as a function of time in the course of controlled  
791 potential electrolysis estimated by GC analysis of the headspace  
792 of the electrolysis cell shows a gradual buildup of CO in the  
793 course of the electrolysis (Figure S119 in the Supporting  
794 Information). A comparison with the performance of [MnBr-  
795 (CO)<sub>3</sub>(bpy)] catalyst investigated under identical conditions  
796 (see Figure S19) shows that the efficiency of CO production  
797 for the new catalysts 1–5 is comparable to that of  
798 [MnBr(CO)<sub>3</sub>(bpy)], with the least sterically hindered  
799 MnIMP complex being somewhat more efficient. Due to the  
800 large volumes used in the experiment, considerable secondary  
801 processes occur during bulk electrolysis, manifested in the loss  
802 of the initial intense yellow-red color of the solution as the  
803 reaction progressed, which was concomitant with an increase in  
804 current toward the end of the electrolysis. These deviations  
805 from an ideal behavior suggest that, as CO<sub>2</sub> is depleted in  
806 solution, competing catalyst degradation pathways begin to  
807 occur, precluding reliable estimates of efficiencies.

808 Estimation of efficiency from the CV data was done by the  
809 relative  $i_{\text{cat}}/i_{\text{p}}$  values (Table S1 in the Supporting Information)  
810 following the method described in refs 4 and 7. Comparing the  
811 current values detected in the CV at  $-2.24$  V (vs Fc/Fc<sup>+</sup>)  
812 recorded under a CO<sub>2</sub> and N<sub>2</sub> atmosphere in acetonitrile/water  
813 also shows that the performances of 1–5 are comparable to one  
814 another and are comparable to that of [Mn(CO)<sub>3</sub>(bpy)Br], at  
815 30–60% efficiency. It is important that the most sterically  
816 protected complexes, MnDIPIMP and MnTBIEP, seem to be  
817 performing better as far as  $i_{\text{cat}}/i_{\text{p}}$  values are concerned but that  
818 the least sterically hindered complex, MnIMP, is the most  
819 efficient in the series. These observations are different from the  
820 observation of MnTBIMP producing more CO than [Mn-  
821 (bpy)(CO)<sub>3</sub>Br] in the bulk electrolysis/GC experiments. While  
822 these data can only be considered in relative terms, they do  
823 show the potential of these complexes to act as a test bed for  
824 optimizing steric vs electronic effects in CO<sub>2</sub> reduction,  
825 whereby the thermodynamic factors, the rate of CO<sub>2</sub>  
826 coordination, and the rate of decomposition of catalyst  
827 precursor species need to be balanced.

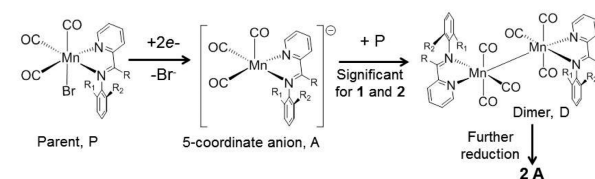
828 The main transformation pathways of 1–5 upon reduction  
829 under an inert atmosphere, and under an atmosphere of CO<sub>2</sub>,  
830 are summarized schematically in Figure 14.

## 831 CONCLUSIONS

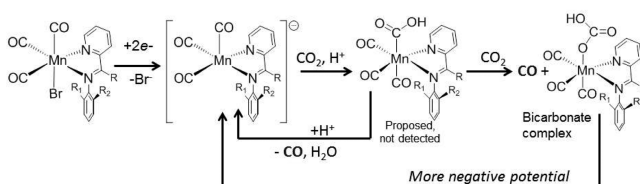
832 A series of Mn(I) tricarbonyl electrocatalysts for CO<sub>2</sub> reduction  
833 which employ, for the first time, asymmetric  $\alpha$ -diimine ligands,  
834 imino-pyridines, has been developed, and their catalytic activity  
835 has been confirmed and evaluated in detail.

836 We have demonstrated through conventional and thin-layer  
837 cyclic voltammetry, UV–vis and IR spectroscopy, and DFT  
838 computational analysis the  $\pi$  decoupling of the phenyl from the  
839 Mn(pyridine-CCN) metallacycle. The practical effect of this  
840 feature is the ability to disentangle steric and electronic effects  
841 of the  $\alpha$ -diimine ligand on the catalytic properties. Until now,  
842 introduction of sterically bulky groups, which are also typically  
843 electron donating, was coming at the price of an increased  
844 overpotential required for CO<sub>2</sub> reduction. The use of an  
845 asymmetric  $\alpha$ -diimine has allowed us to probe the effect of  
846 adding ever greater sterically demanding groups without much

### (a) inert atmosphere



### (b) CO<sub>2</sub> atmosphere



**Figure 14.** Main transformation pathways of 1–5 upon reduction under (a) an inert atmosphere and (b) an atmosphere of CO<sub>2</sub>. A is detected for 3 only due to the comparatively slower reaction of [3]<sup>−</sup> with CO<sub>2</sub>.

change in the catalytic potential. We have demonstrated that a  
systematic increase in the steric hindrance of the R<sub>1</sub> and R<sub>2</sub>  
groups in the IMP subseries results in the switch of the nature  
of the first reduction product detected on the time scale of the  
experiment under an inert gas atmosphere, from a dimer to a  
five-coordinate anion, at a very similar reduction potential. In  
the absence of sterically hindering groups on the phenyl ring,  
MnIMP, a dimer is formed, while increasing the steric  
hindrance by adding <sup>t</sup>Pr groups to the R<sub>1</sub> and R<sub>2</sub> positions  
(MnDIPIMP) resulted in direct formation of the five-  
coordinate anion, in line with prior observations for similar  
sterically hindered ligands.<sup>23,26</sup> MnIPIMP (in which case the  
dimer may be reduced at the parent cathodic wave due to  
slightly negatively shifted reduction potential vs that for  
MnIMP) exhibited behavior intermediate to that of MnIMP  
and MnDIPIMP with both the dimer and the five-coordinate  
anion observed to be formed concurrently. MnTBIMP and  
MnTBIEP both formed the five-coordinate anion directly upon  
reduction of the parent complex.

Under a CO<sub>2</sub> atmosphere, all of the complexes reduce CO<sub>2</sub>  
to CO. The buildup of CO in the thin-layer spectroelectro-  
chemical cell resulted in the displacement of the  $\alpha$ -diimine  
ligand, forming [Mn(CO)<sub>5</sub>]<sup>−</sup>. The complex containing the  
most sterically demanding ligand, DIPIMP, is as anticipated  
least susceptible to  $\alpha$ -diimine displacement with CO, forming  
exclusively the five-coordinate anion upon the first reduction;  
it also has the least propensity to coordinate CO<sub>2</sub>, resulting in a  
considerable buildup of the concentration of the five-coordinate  
anion. An intermediate formation of the bicarbonate is also  
likely, as a band at 1686 cm<sup>−1</sup> is present at intermediate times.  
Of particular interest is that the least sterically hindered  
complex, MnIMP, seemed to form a CO<sub>2</sub>-associated complex  
directly upon the first reduction, with no significant formation  
of the dimer being observed on the time scale of the  
experiment. This behavior is similar to that reported for the  
symmetric nonaromatic Mn-R-DAB (R = alkyl) compounds.<sup>8,30</sup>  
The formation of a stable bicarbonate complex, either through  
the coordination to the metal center or via the imino C=N  
bond,<sup>23,37</sup> leads to the need for increased overpotential. From  
that point of view, the steric hindering (protection) of the  
metal center/the imino C=N bond in the Mn(IP) complexes  
is advantageous, as it disfavors the Mn–Mn dimerization (when

889 MnIMP is compared with MnDIPIMP). However, such steric  
890 crowding also slows the catalytic conversion of CO<sub>2</sub> to CO at  
891 the negative overpotentials, as can be seen in the GC data and  
892 from the  $i_{\text{cat}}/i_p$  values. A difference in the reactivity of  
893 MnTBIMP and MnTBIEP, where no dimer formation has  
894 been detected for either of the complexes in the IR-SEC  
895 experiments but where MnTBIEP exhibits slower CO<sub>2</sub>  
896 conversion due to R = CH<sub>3</sub>, alters the HOMO–LUMO gap  
897 in comparison to the IMP series as well as introduces additional  
898 steric bulk, further supporting the notion that it is possible to  
899 separate steric and electronic factors to a large extent. Balancing  
900 these factors by careful ligand design may lead to the optimal  
901 solution.

902 The new family of CO<sub>2</sub> reduction catalysts presents an  
903 exciting platform for versatile and relatively independent tuning  
904 of steric and electronic properties, offering a far greater  
905 tunability in comparison to catalysts with aromatic bpy-based or  
906 nonaromatic R-DAB-based ligands and abundant options to  
907 refine and optimize Mn tricarbonyl CO<sub>2</sub> reduction catalysts.

## 908 ■ ASSOCIATED CONTENT

### 909 ● Supporting Information

910 The Supporting Information is available free of charge on the  
911 ACS Publications website at DOI: 10.1021/acs.inorg-  
912 chem.6b01477.

913 Calculated frontier orbitals from HOMO-3 to LUMO+3  
914 for all studied complexes, complete CV measurements,  
915 control experiments, crystallographic data, and <sup>1</sup>H NMR  
916 spectra of the new complexes (PDF)

917 Crystallographic data (CIF)

918 Crystallographic data (CIF)

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### 926 Notes

927 The authors declare no competing financial interest.

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973 DAB = 1,4-Diisopropyl-1,4-diaza-1,3-butadiene) at Variable Temper-  
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