

## Electron-transfer-catalysed Carbonyl Substitution in [(Arene)Mn(CO)<sub>3</sub>]<sup>+</sup> Complexes

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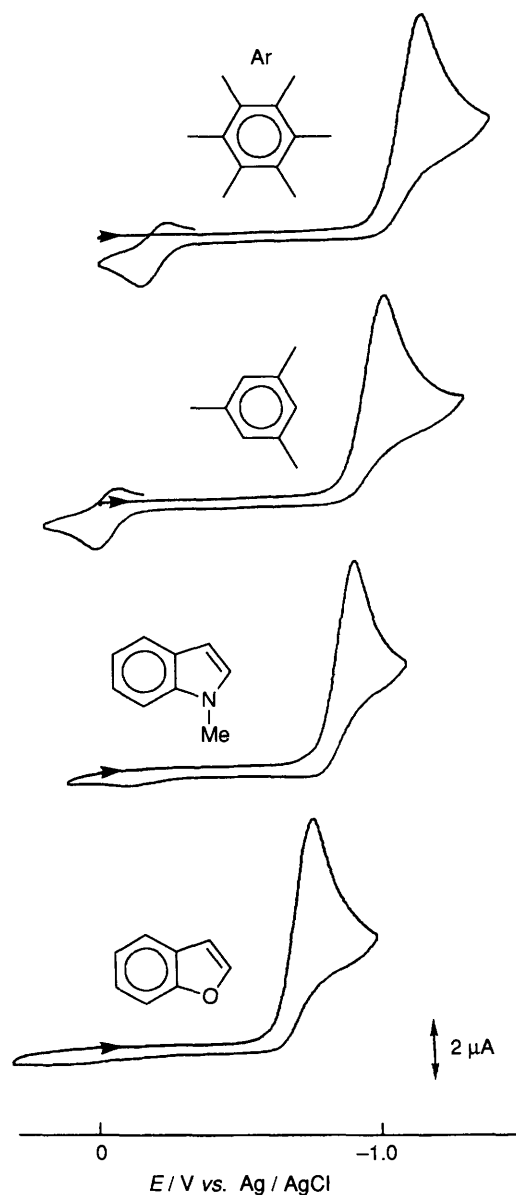
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Electrochemical reduction of [(arene)Mn(CO)<sub>3</sub>]<sup>+</sup> in the presence of tertiary phosphites or phosphines (L) produces [(arene)Mn(CO)<sub>2</sub>L]<sup>+</sup> via electron-transfer catalysis; [(mesitylene)Re(CO)<sub>3</sub>]<sup>+</sup> is reduced in a two-electron chemically reversible step and does not undergo ligand substitution.

The reductive activation of organometallic complexes to ligand substitution has been demonstrated for a variety of polynuclear and several mononuclear complexes.<sup>1-10</sup> Herein we report that in the presence of some phosphorus nucleophiles, [(arene)Mn(CO)<sub>3</sub>]<sup>+</sup> undergoes clean electrocatalytic CO substitution to afford [(arene)Mn(CO)<sub>2</sub>L]<sup>+</sup>. In sharp contrast to this behaviour, the rhenium analogues do not undergo ligand substitution upon reduction.

The electrochemical reduction of [(arene)Mn(CO)<sub>3</sub>]<sup>+</sup> (**1**<sup>+</sup>) in CH<sub>2</sub>Cl<sub>2</sub> under N<sub>2</sub> was found to be chemically irreversible at 20 °C and scan rates up to 20 V s<sup>-1</sup> for a range of arenes: C<sub>6</sub>H<sub>6</sub> (**1a**<sup>+</sup>), 1,3,5-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub> (**1b**<sup>+</sup>), 1,3,5-C<sub>6</sub>H<sub>3</sub>Et<sub>3</sub> (**1c**<sup>+</sup>), C<sub>6</sub>Me<sub>6</sub> (**1d**<sup>+</sup>), C<sub>6</sub>Et<sub>6</sub> (**1e**<sup>+</sup>), *N*-methylindole (**1f**<sup>+</sup>) and benzofuran (**1g**<sup>+</sup>). Fig. 1 presents typical results. The cyclic voltammograms (CVs) for complexes **1a-d**<sup>+</sup> but not **1e-g**<sup>+</sup>

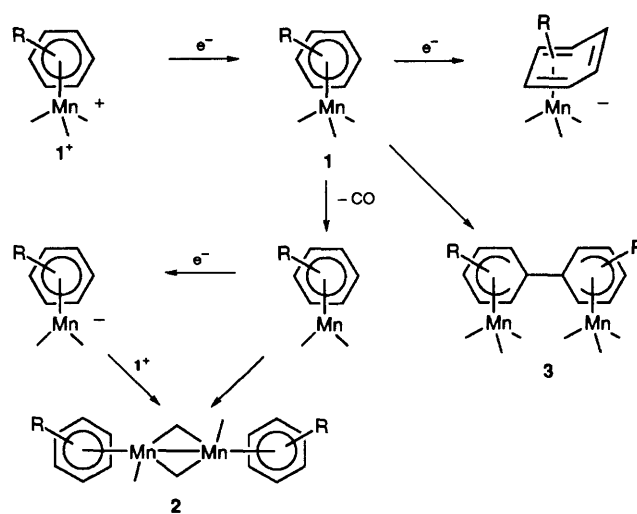
have a reversible couple near 0 V that is due to a product of the primary reduction near -1 V. IR-OTTLE (optically transparent thin-layer electrode) experiments with **1d**<sup>+</sup> suggested that the reduction product is the dimer [{"(C<sub>6</sub>Me<sub>6</sub>)Mn(CO)<sub>2</sub>}]<sub>2</sub> **2d**, which was originally discovered by Eyman *et al.*<sup>11</sup> Proof that the reversible couple in the CVs is due to this type of dimer formation in the reduction of **1a-d**<sup>+</sup> was provided by the IR and CV characteristics of genuine samples of **2a-d**. Under a CO atmosphere and/or at -40 °C, the formation of **2d** from **1d**<sup>+</sup> was inhibited and the primary reduction wave showed partial chemical reversibility, along with an increase in current from *n* = 1 to *n* = ca. 1.3. The reduction of **1e-g**<sup>+</sup> consumed one electron and did not lead to **2**; IR-OTTLE experiments showed the absence of **2** and suggested that the chemical irreversibility is due to radical



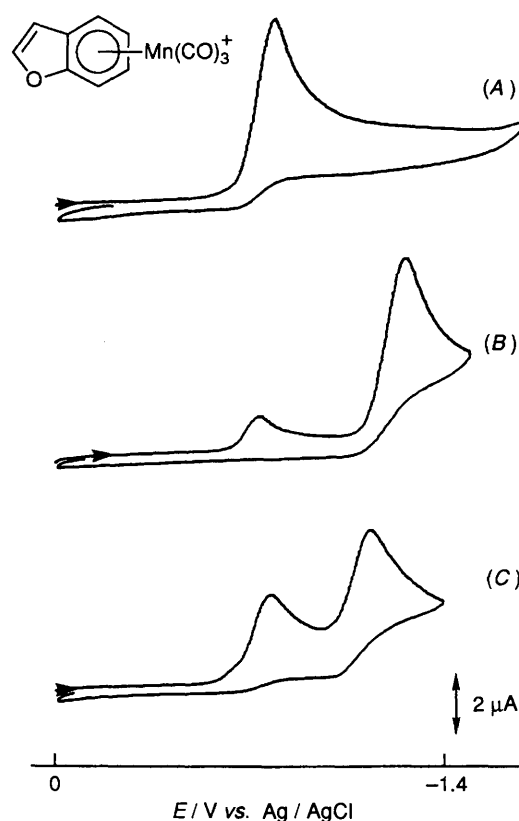
**Fig. 1** CVs of  $1.0 \text{ mol dm}^{-3}$   $[(\text{arene})\text{Mn}(\text{CO})_3]\text{PF}_6$  in  $\text{CH}_2\text{Cl}_2$ - $0.10 \text{ mol dm}^{-3}$   $\text{Bu}_4\text{NPF}_6$  at 293 K. The arene is indicated above each CV. The working electrode was a 1.0 mm diameter platinum disk and the scan rate was  $0.50 \text{ V s}^{-1}$ . All potentials are relative to ferrocene  $E_1 = 0.52 \text{ V}$ .

coupling through the arene rings to give cyclohexadienyl (Ch) complexes  $[\{(\text{Ch})\text{Mn}(\text{CO})_3\}_2]$  **3** analogous to ones prepared *via* chemical reduction.<sup>12</sup> The lack of any observable oxidation wave for **3** is expected based on observations with monomeric  $[(\text{Ch})\text{Mn}(\text{CO})_3]$  complexes.<sup>13</sup>

A plausible mechanism for the electrochemical reduction of **1**<sup>+</sup> is given in Scheme 1. The 19-electron  $[(\text{arene})\text{Mn}(\text{CO})_3]$  can dissociate CO followed by dimerization to **2** or reduction to the known<sup>11,14</sup>  $[(\text{arene})\text{Mn}(\text{CO})_2]^-$  anion, which is expected<sup>11</sup> to react rapidly with the starting complex **1**<sup>+</sup>. Computer simulation<sup>15,16</sup> of this dissociative part of the mechanism quantitatively reproduced the CVs for **1a-d**<sup>+</sup> at 20 °C under  $\text{N}_2$ . Under CO or at low temperature the CO dissociation from **1** is inhibited and direct dimerization to **3** or subsequent reduction to the  $\eta^4$ -arene complex competes with the formation of **2**. It is known<sup>12,17</sup> that chemical reduction of **1**<sup>+</sup> under certain conditions can generate **3** or the  $\eta^4$ -arene complex. Apparently, complexes **1e-g**<sup>+</sup> follow the reduction route directly to **3** without forming substantial amounts of **2** or  $\eta^4$ -arene.

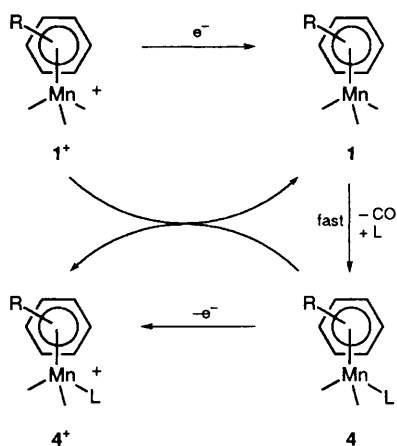


**Scheme 1**



**Fig. 2** CVs of  $1.0 \text{ mol dm}^{-3}$   $[(\text{benzofuran})\text{Mn}(\text{CO})_3]\text{BF}_4$  in  $\text{CH}_2\text{Cl}_2$ - $0.10 \text{ mol dm}^{-3}$   $\text{Bu}_4\text{NPF}_6$  at 293 K in the presence of (A) no nucleophile, (B)  $1.5 \text{ mol dm}^{-3}$   $\text{P}(\text{O}i\text{Bu})_3$  and (C)  $3.0 \text{ mol dm}^{-3}$   $\text{PPh}_3$ . The working electrode was a 1.0 mm diameter platinum disk and the scan rate was  $0.50 \text{ V s}^{-1}$ . All potentials are relative to ferrocene  $E_1 = 0.52 \text{ V}$ .

In the presence of tri-*n*-butyl phosphite,  $\text{P}(\text{O}i\text{Bu})_3$ , the reduction of **1**<sup>+</sup> led to efficient electrocatalytic CO substitution to produce  $[(\text{arene})\text{Mn}(\text{CO})_2(\text{P}(\text{O}i\text{Bu})_3)]^+$  (**4**<sup>+</sup>). No reaction occurred on the time scale of the experiments unless a reducing potential was applied. All of the **1**<sup>+</sup> complexes reacted cleanly with  $\text{P}(\text{O}i\text{Bu})_3$  in this manner except **1e**<sup>+</sup>, which showed no reaction. The heterocyclic arene complexes **1f**<sup>+</sup> and **1g**<sup>+</sup>, but not complexes **1a**<sup>+</sup>-**1e**<sup>+</sup>, also underwent CO substitution in the presence of low concentrations of  $\text{PPh}_3$ . Fig. 2 shows typical CVs for **1g**<sup>+</sup> and Scheme 2 gives the mechanism. As **1**<sup>+</sup> is reduced to **1**, rapid CO substitution



Scheme 2

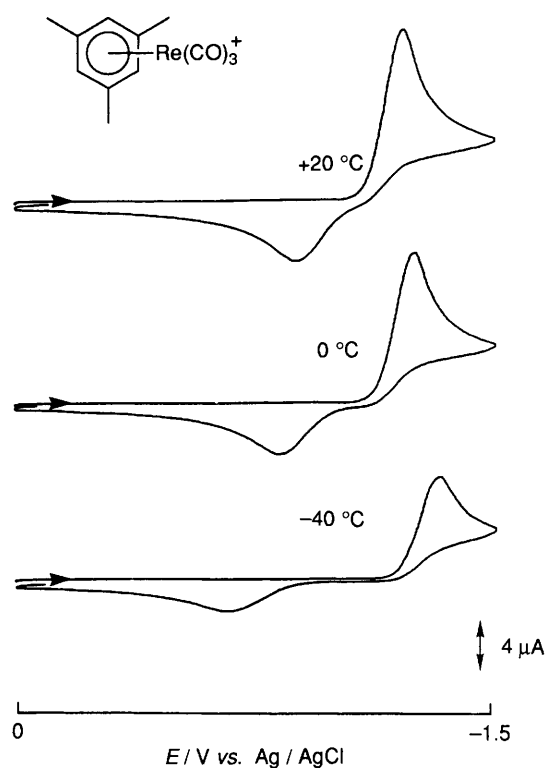


Fig. 3 CVs of  $1.0 \text{ mol dm}^{-3}$  [(mesitylene) $\text{Re}(\text{CO})_3$ ] $\text{PF}_6$  in  $\text{CH}_2\text{Cl}_2$ - $0.10 \text{ mol dm}^{-3}$   $\text{Bu}_4\text{NPF}_6$ . The working electrode was a  $1.0 \text{ mm}$  diameter glassy carbon disk and the scan rate was  $0.50 \text{ V s}^{-1}$ . All potentials are relative to ferrocene  $E_1 = 0.52 \text{ V}$ .

occurs to give **4**, which is spontaneously oxidized either at the electrode to give **4<sup>+</sup>** or *via* reaction with **1<sup>+</sup>** to afford **4<sup>+</sup>** and regenerate **1**. The process is catalytic because **4<sup>+</sup>** is reduced at a more negative potential than is **1<sup>+</sup>** (the more negative wave in Fig. 2). IR experiments showed that the overall conversion **1<sup>+  $\rightarrow$  **4<sup>+</sup>** is quantitative. Typically, the passage of charge corresponding to 3% of the amount of **1<sup>+</sup>** present was sufficient to effect complete conversion to **4<sup>+</sup>** with  $\text{P}(\text{O}i\text{Bu})_3$  as the nucleophile ( $[\mathbf{1}^+] = 1 \text{ mmol dm}^{-3}$ ;  $[\text{P}(\text{O}i\text{Bu})_3] = 1.5 \text{ mmol dm}^{-3}$ ). CV data showed that the reactivity with  $\text{P}(\text{O}i\text{Bu})_3$  depends on the arene in the order benzofuran  $>$   $1,3,5\text{-C}_6\text{H}_3\text{Me}_3 >$   $1,3,5\text{-C}_6\text{H}_3\text{Et}_3 \gg \text{C}_6\text{Et}_6$ .</sup>**

The behaviour of [(mesitylene) $\text{Re}(\text{CO})_3$ ] $^+$  **5<sup>+</sup>** is in marked contrast to that of manganese analogue, **1b<sup>+</sup>**. CVs at a glassy carbon electrode (Fig. 3) suggested that the reduction occurs in a two-electron chemically reversible step; double potential

step chronoamperometry and steady-state voltammetry with  $5 \mu\text{m}$  and  $2 \mu\text{m}$  diameter platinum disk microelectrodes verified the chemical reversibility and that  $n = 2$ . The presence of  $\text{CO}$ ,  $\text{P}(\text{O}i\text{Bu})_3$  or  $\text{P}i\text{Bu}_3$  had no effect on the CVs. The large cathodic and anodic peak separations in Fig. 3 indicate a slow heterogeneous charge transfer step. The most likely interpretation is that **5<sup>+</sup>** is reduced to **5**, which undergoes a slow and spontaneous second reduction as the arene slips from  $\eta^6$  to  $\eta^4$ . A variety of arene complexes, especially with heavier transition metals, show a similar type of behaviour.<sup>18</sup>

The conclusion is that [(arene) $\text{Mn}(\text{CO})_3$ ] $^+$  complexes are activated to CO dissociation (substitution) upon one-electron reduction, whereas the rhenium analogues do not undergo CO dissociation, preferring instead arene ring slippage ('dissociation') in conjunction with the (spontaneous) addition of a second electron to give the 18-electron  $\eta^4$ -arene complex **5<sup>-</sup>**.

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