Supporting Information

Electrocatalytic Reduction of Low Concentration CO₂

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Fig. S1. Curve fitting of the FT-IR spectrum of the Re(I) complexes (5.0 mM) in a DMF-TEOA (5:1 v/v) solution containing 0.1 M Et₄NBF₄ after purging with 1% CO₂. Black asterisk (*), blue triangle (▲) and red circle (●) display the peaks attributed to Re-DMF⁺, Re-TEOA, and Re-CO₂TEOA, respectively.
Fig. S2. CVs of the Re(I) complex (0.5 mM) in DMF (a) and in a DMF-TEOA mixed solution (5:1 v/v) (b) containing Et$_4$NBF$_4$ (0.1 M) as supporting electrolyte under an Ar atmosphere at a sweep rate of 200 mV s$^{-1}$. A glassy carbon electrode (diameter: 3 mm), a Ag/AgNO$_3$ (10 mM) electrode and a Pt wire were used as working, reference, and counter electrode, respectively.

Fig. S3. Picture of the setup for the bulk electrolysis. The right side is the cathodic chamber for CO$_2$ reduction reaction.
Fig. S4. Time courses of current during bulk electrolysis using the Re(I) catalyst (0.5 mM) at −1.82 V in a DMF-TEOA solution containing Et₄NBF₄ (0.1 M) under (a) 100%, (b) 10%, and (c) 1% CO₂ atmospheres (10 mL min⁻¹).
Fig. S5. Time courses of current during bulk electrolysis using Re-DMF⁺ (0.5 mM) at −1.82 V in a DMF solution containing Et₄NBF₄ (0.1 M) under (a) 100% and (b) 1% CO₂ atmospheres (10 mL min⁻¹).
**Fig. S6.** (a) FT-IR spectra, (b) CVs, and (c) UHPLCs of the Re(I) complexes before and after the bulk electrolysis at -1.82 V under a 1% CO$_2$ atmosphere in DMF containing Et$_4$NBF$_4$ (0.1 M) as supporting electrolyte; black lines: before electrolysis, and red lines: after electrolysis. The blue line in (c) is UHPLC of Re-OCHO. The FT-IR spectra and CVs were measured by using the reaction solutions without any treatment. UHPLC: an ODS column: $\lambda_{det} = 400$ nm, a MeOH-H$_2$O mixed solution containing KH$_2$PO$_4$ buffer of pH5.9 (1:1 v/v) was used as the eluent. The blue line shows the analysis result of the isolated Re-OCHO as reference.
Fig. S7. FT-IR spectra (black) before and (red) after adding TPAHBF₄ (25 mM) into a DMF solution containing Re-DMF⁺ (5.0 mM) and Et₄NBF₄ (0.1 M) under an Ar atmosphere.

Fig. S8. Time courses of current during bulk electrolysis using Re-DMF⁺ (0.5 mM) at −1.82 V in the DMF solution containing Et₄NBF₄ (0.1 M) and TPAHBF₄ (25 mM) under (a) 100% and (b) 1% CO₂ atmospheres (10 mL min⁻¹).
Fig. S9. (a) FT-IR spectra, (b) CVs, and (c), UHPLCs of the Re(I) complexes before and after the bulk electrolysis at -1.82 V under a 10% CO$_2$ atmosphere a DMF-TEOA mixed solution (5:1 v/v) containing Et$_4$NBF$_4$ (0.1 M) as supporting electrolyte; black lines: before electrolysis, and red lines: after electrolysis. The blue line in (c) is UHPLC of Re-OCHO. The FT-IR spectra and CVs were measured by using the reaction solutions without any treatment. UHPLC: an ODS column: $\lambda_{\text{det}} = 400$ nm, a MeOH-H$_2$O mixed solution containing KH$_2$PO$_4$ buffer of pH5.9 (1:1 v/v) was used as the eluent. The blue line shows the analysis result of the isolated Re-OCHO as reference.