Diiron hexacarbonyl complexes as potential CO-RMs: their CO-releasing initiated by
the substitution reaction with cysteamine and structural correlation to the bridging
linkage

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Fig. S1 Infrared spectral variation during the CO-releasing process of complex 3 ([3] = 0.011 mol L\(^{-1}\) and [CysA] = 0.066 mol L\(^{-1}\)) (top) and the intermediates in the reaction mixture (bottom), when the reaction proceeded from 1 min to 7 min in
DMSO at 37 °C.

Fig. S2 Infrared spectral variation during the CO-releasing process of complex 4 ([4] = 0.011 mol L\(^{-1}\) and [CysA] = 0.066 mol L\(^{-1}\)) (top) and the intermediates in the
reaction mixture (bottom), when the reaction proceeded for 1 min (4-1), 3 min (4-2) and 7 min (4-3), respectively, in DMSO at 37 °C.

Fig. S3 Infrared spectral variation during the CO-releasing process of complex 7 ([7]
= 0.011 mol L\(^{-1}\) and \([\text{CysA}] = 0.066\) mol L\(^{-1}\) (top) and the intermediates in the reaction mixture (bottom), when the reaction proceeded for 260 min (7-1) and 320 min (7-2), respectively, in DMSO at 37 °C.

Fig. S4 Infrared spectral variation during the CO-releasing process of complex 8 ([8]
= 0.011 mol L\(^{-1}\) and [CysA] = 0.066 mol L\(^{-1}\)) (top) and the intermediates in the reaction mixture (bottom), when the reaction proceeded for 260 min (8-1) and 320 min (8-2), respectively, in DMSO at 37 °C.

Fig. S5 Infrared spectral variation during the CO-releasing process of complex 9 ([9]
= 0.011 mol L\(^{-1}\) and \([\text{CysA}] = 0.066 \text{ mol L}^{-1}\) (top) and the intermediates in the reaction mixture (bottom), when the reaction proceeded for 70 min (9-1) and 235 min (9-2), respectively, in DMSO at 37 °C.

Fig. S6 \(^1\)H NMR spectra of the final decomposition product for complex 4 (CD\(_3\)Cl).
Fig. S7 $^{13}$C NMR spectra of the final decomposition product for complex 4 (CD$_3$Cl).

Fig. S8 Mass spectra of the final decomposition product for complex 4 (ESI, cation; the final decomposition product was obtained via the reaction of complex 4 with 6 equivalents of CysA under inert atmosphere at room temperature for 24 h).
Table S1 DFT calculation results and the $k_{obs}$ of the compounds

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<tr>
<th>Complex</th>
<th>Metal centre</th>
<th>$k_{obs}$</th>
<th>NAP charges (e)</th>
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<tbody>
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<td>8</td>
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<td>-3.25846</td>
</tr>
</tbody>
</table>

Scheme S1 Possible pathways of substitution-initiated CO-releasing from complex 4 by CysA under inert atmosphere $^{41}$. 