**Supporting Information for**

# Homoleptic and heteroleptic Au(I) complexes containing the new $[Co_5C(CO)_{12}]^-$ cluster as ligand

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**Figure S.1**

*Cyclic (green, black and red) and hydrodynamic (blue) voltammograms recorded at a platinum electrode in a $CH_2Cl_2$ solution of $[\{Co_5C(CO)_{12}\}_2Au]^-$, **[2]**$^-$. $[N^nBu_4][PF_6]$ (0.2 mol dm$^{-3}$) as supporting electrolyte. Scan rates: 0.1 V s$^{-1}$.*

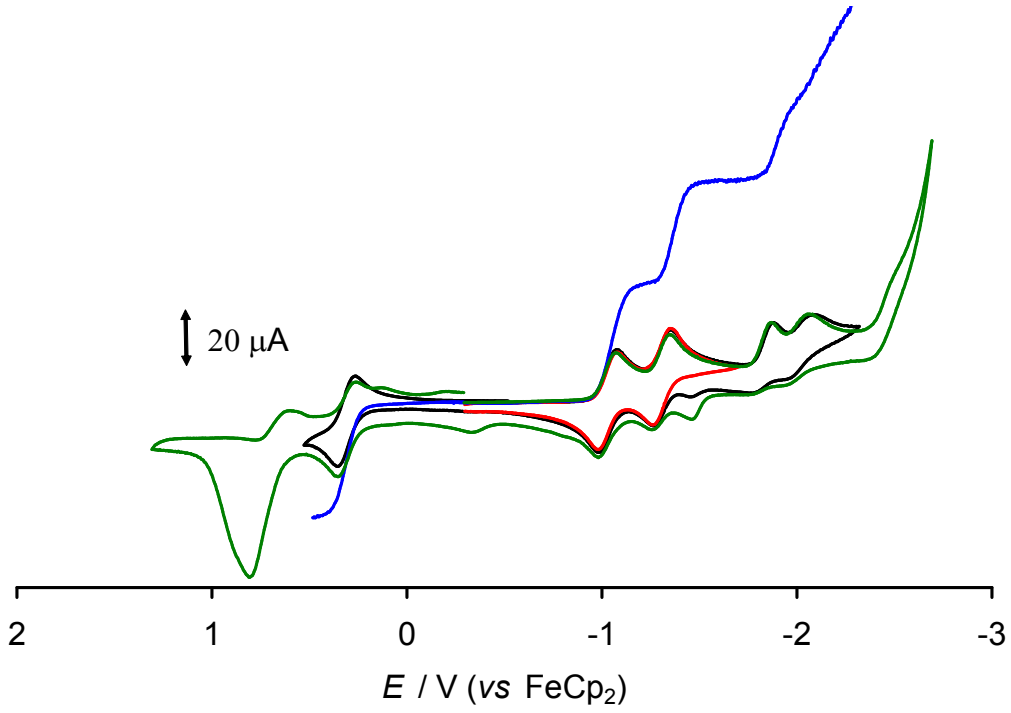


**Table S.1**

*ν(CO) stretching frequencies (cm$^{-1}$) of **[2]**$^{n-}$ (n = 0-3) as obtained from spectroelectrochemical experiments in $CH_2Cl_2$ solution.*

| | |
|---|---|
| **2** | 2062(s), 2047(s), 1872(m) |
| **[2]**$^-$ | 2060(m), 2043(s), 2012(m), 1856(m) |
| **[2]**$^{2-}$ | 2027(s), 1982(m), 1838(sh), 1814(m) |
| **[2]**$^{3-}$ | 1993(s), 1957(m), 1787(m) |

**Figure S.2**

*Selected IR spectra recorded in a OTTLE cell during the electrolysis of $[\{Co_5C(CO)_{12}\}_2Au]^-$, in $CH_2Cl_2$ solution containing $[N^nBu_4][PF_6]$ 0.2 mol $dm^{-3}$ as the supporting electrolyte, and corresponding to the different charged clusters $[\{Co_5C(CO)_{12}\}_2Au]$/$[\{Co_5C(CO)_{12}\}_2Au]^-$ /$[\{Co_5C(CO)_{12}\}_2Au]^{2-}$/$[\{Co_5C(CO)_{12}\}_2Au]^{3-}$.*

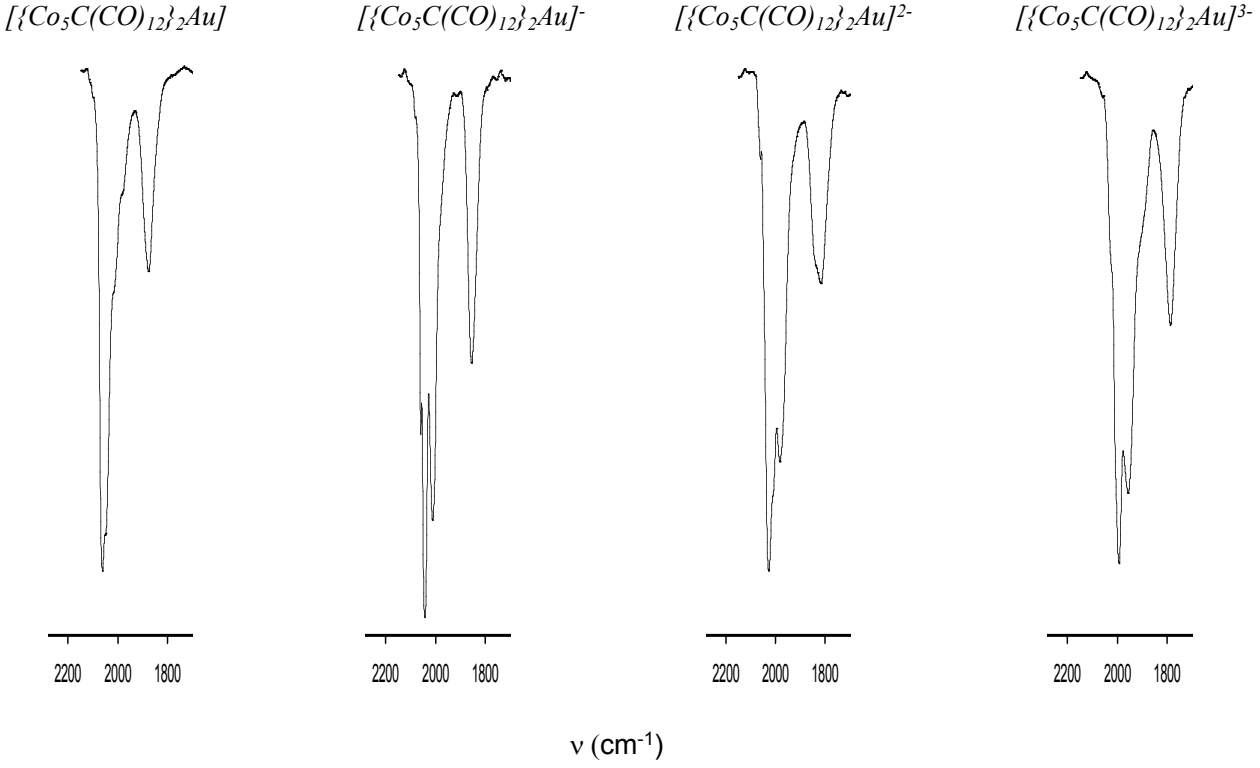


**Table S.2.**

*ν(CO) stretching frequencies ($cm^{-1}$) of **[1]**$^{n-}$ (n = 1-3) as obtained from spectroelectrochemical experiments in $CH_2Cl_2$ solution.*

| | |
|---|---|
| **[1]**$^{-}$ | 2030(s), 2013(m), 1973(w), 1851(m) |
| **[1]**$^{2-}$ | 2021(w), 1983(s), 1960(sh), 1800(m) |
| **[1]**$^{3-}$ | 2026(w), 1918(s), 1758(m) |

**Figure S.3**

*Selected IR spectra recorded in a OTTLE cell during the electrolysis of $[\{Co_5C(CO)_{12}\}Au\{Co(CO)_4\}]^-$, in $CH_2Cl_2$ solution containing $[N^nBu_4][PF_6]$ 0.2 mol $dm^{-3}$ as the supporting electrolyte, and corresponding to the different charged clusters $[\{Co_5C(CO)_{12}\}Au\{Co(CO)_4\}]^-$/$[\{Co_5C(CO)_{12}\}Au\{Co(CO)_4\}]^{2-}$/$[\{Co_5C(CO)_{12}\}Au\{Co(CO)_4\}]^{3-}$.*