# Supporting Information:

# The nature and degree of the cooperativity of ($\eta^5$-$C_5H_5$)-metal and metal-CO bonds in half-sandwich complexes of groups 5, 7, 9, and 11 transition metals

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## Contents

* The following equations demonstrate how to calculate the bond dissociation energy of A–B, B–C, A–BC and AB–C bonds:

$$-BDE_{A-B} = E_{AB} - (E_A + E_B) \quad \text{(S1)}$$

$$-BDE_{B-C} = E_{BC} - (E_B + E_C) \quad \text{(S2)}$$

$$-BDE_{A-BC} = E_{ABC} - (E_A + E_{BC}) \quad \text{(S3)}$$

$$-BDE_{AB-C} = E_{ABC} - (E_{AB} + E_C) \quad \text{(S4)}$$

The following equations demonstrate how to calculate the interaction energies of A–B, B–C, A–BC and AB–C bonds in the structure of an ABC system:

$$IE_{A-B}^{ABC} = E_{AB} - \left(E_A^{ABC} + E_B^{ABC}\right) \quad \text{(S5)}$$

$$IE_{B-C}^{ABC} = E_{BC} - \left(E_B^{ABC} + E_C^{ABC}\right) \quad \text{(S6)}$$

$$IE_{A-BC}^{ABC} = E_{ABC} - \left(E_A^{ABC} + E_{BC}^{ABC}\right) \quad \text{(S7)}$$

$$IE_{AB-C}^{ABC} = E_{ABC} - \left(E_{AB}^{ABC} + E_C^{ABC}\right) \quad \text{(S8)}$$

In the above equations, $E_{ABC}$, $E_{AB}$ $E_{BC}$, and $E_A$, $E_B$, and $E_c$ represent the electronic energies of ABC, AB, BC, A, B, and C, respectively, in their optimized geometries. Meanwhile, $E_{AB}^{ABC}$, $E_{BC}^{ABC}$, $E_A^{ABC}$, $E_B^{ABC}$ and $E_C^{ABC}$ denote the electronic energies of AB, BC, A, B and C when frozen in the optimized geometry of ABC.

The calculated BDEs and IEs were subsequently employed in determining the stabilization- and interaction-based cooperative energies within an ABC system. It has been demonstrated that the mutual impacts of chemical bonds can be evaluated by comparing both bond dissociation energies and interaction energies [Ref. 26]. The stabilization-based cooperativity ($E_{coop}$) is calculated using the following equations:

$$\Delta BDE_{A-B} = BDE_{A-B} - BDE_{A-BC} \quad \text{(S9)}$$

$$\Delta BDE_{B-C} = BDE_{B-C} - BDE_{AB-C} \quad \text{(S10)}$$

$$E_{coop} = \Delta BDE_{A-B} = \Delta BDE_{B-C} \quad \text{(S11)}$$

The interaction-based cooperativity ($\Delta IE_{coop}$), on the other hand, is calculated using the following equations [Ref. 26].

$$\Delta IE_{A-B} = IE_{A-BC}^{ABC} - IE_{A-B}^{ABC} \quad \text{(S12)}$$

$$\Delta IE_{B-C} = IE_{AB-C}^{ABC} - IE_{B-C}^{ABC} \quad \text{(S13)}$$

$$\Delta IE_{coop} = \Delta IE_{A-B} = \Delta IE_{B-C} \quad \text{(S14)}$$

In the above equations, the ABC superscript indicates that the interactions are calculated in the optimized geometry of ABC system. In contrast to the stabilization-based approach, this method does not require the optimization of all individual fragments. Indeed, even when there is no information about the independent structures of A, B, and C fragments, such as when a fragment is unstable, the mutual impact of A–B and B–C interactions can still be assessed within the ABC system.

**Table S1**. Calculated values for interaction energies (IE, kcal/mol) between the defined fragments frozen in the optimized geometry of the complexes studied here, and related, $\Delta IE_{coop}$[a], $\%\Delta IE_{A-B}$ and $\%\Delta IE_{B-C}$ values[b] in [($\eta^5$-Cp)Cu(CO)] complex, at 24 levels of theory.

| Methods | $IE_{A-B}^{ABC}$ | $IE_{A-BC}^{ABC}$ | $IE_{B-C}^{ABC}$ | $IE_{AB-C}^{ABC}$ | $\Delta IE_{coop}$[a] | $\%\Delta IE_{A-B}$[b] | $\%\Delta IE_{B-C}$[b] |
|---|---|---|---|---|---|---|---|
| **B3LYP** | | | | | | | |
| LanL2DZ | -188.38 | -195.35 | -38.11 | -45.08 | -6.97 | 4% | 18% |
| def2-SVP | -189.93 | -200.74 | -36.75 | -47.56 | -10.81 | 6% | 29% |
| def2-TZVP | -187.03 | -195.00 | -35.11 | -43.08 | -7.97 | 4% | 23% |
| def-QZVP | -185.23 | -192.92 | -35.21 | -42.90 | -7.69 | 4% | 22% |
| **B971** | | | | | | | |
| LanL2DZ | -188.84 | -196.76 | -36.69 | -44.61 | -7.92 | 4% | 22% |
| def2-SVP | -190.10 | -202.26 | -35.11 | -47.27 | -12.16 | 6% | 35% |
| def2-TZVP | -188.83 | -197.96 | -34.47 | -43.60 | -9.13 | 5% | 26% |
| def-QZVP | -187.09 | -195.76 | -34.65 | -43.32 | -8.67 | 5% | 25% |
| **BP86** | | | | | | | |
| LanL2DZ | -195.68 | -205.06 | -45.90 | -55.28 | -9.38 | 5% | 20% |
| def2-SVP | -198.37 | -212.69 | -45.48 | -59.80 | -14.32 | 7% | 31% |
| def2-TZVP | -197.55 | -207.95 | -45.25 | -55.65 | -10.40 | 5% | 23% |
| def-QZVP | -195.94 | -205.70 | -45.50 | -55.26 | -9.76 | 5% | 21% |
| **M06** | | | | | | | |
| LanL2DZ | -194.11 | -200.81 | -39.60 | -46.30 | -6.70 | 3% | 17% |
| def2-SVP | -195.76 | -206.84 | -36.59 | -47.67 | -11.08 | 6% | 30% |
| def2-TZVP | -195.15 | -203.34 | -37.19 | -45.38 | -8.19 | 4% | 22% |
| def-QZVP | -192.55 | -201.12 | -36.32 | -44.89 | -8.57 | 4% | 24% |
| **M06L** | | | | | | | |
| LanL2DZ | -195.95 | -205.30 | -45.50 | -54.85 | -9.35 | 5% | 20% |
| def2-SVP | -194.96 | -211.69 | -40.14 | -56.87 | -16.73 | 9% | 42% |
| def2-TZVP | -199.00 | -210.53 | -44.02 | -55.55 | -11.53 | 6% | 26% |
| def-QZVP | -195.95 | -209.40 | -41.88 | -55.33 | -13.45 | 7% | 32% |
| **CCSD(T)//MP2** | | | | | | | |
| LanL2DZ | -179.09 | -191.97 | -24.80 | -37.68 | -12.88 | 7% | 52% |
| def2-SVP | -182.11 | -192.02 | -28.15 | -38.06 | -9.91 | 5% | 35% |
| def2-TZVP | -184.91 | -202.54 | -22.71 | -40.34 | -17.63 | 9% | 78% |
| def-QZVP | - | - | - | - | - | - | - |

[a] See ref. 26 of the paper. ($\Delta IE_{coop} = \Delta IE_{A-B} = \Delta IE_{B-C}$)

[b] $\%\Delta IE_{A-B} = \frac{|\Delta IE_{coop}|}{IE_{A-B}^{ABC}} \times 100$, $\%\Delta IE_{B-C} = \frac{|\Delta IE_{coop}|}{IE_{B-C}^{ABC}} \times 100$

**Table S2**. Calculated values for interaction energies (IE, kcal/mol) between the defined fragments frozen in the optimized geometry of the complexes studied here, and related, $\Delta IE_{coop}$[a], $\%\Delta IE_{A-B}$ and $\%\Delta IE_{B-C}$ values[b] in [($\eta^5$-Cp)Ag(CO)] complex, at 24 levels of theory.

| Methods | $IE_{A-B}^{ABC}$ | $IE_{A-BC}^{ABC}$ | $IE_{B-C}^{ABC}$ | $IE_{AB-C}^{ABC}$ | $\Delta IE_{coop}$ | $\%\Delta IE_{A-B}$ | $\%\Delta IE_{B-C}$ |
|---|---|---|---|---|---|---|---|
| **B3LYP** | | | | | | | |
| LanL2DZ | -164.68 | -172.67 | -22.89 | -30.88 | -7.99 | 5% | 35% |
| def2-SVP | -170.08 | -178.23 | -24.03 | -32.18 | -8.15 | 5% | 34% |
| def2-TZVP | -163.84 | -172.50 | -22.40 | -31.06 | -8.66 | 5% | 39% |
| def-QZVP | -162.77 | -171.33 | -22.77 | -31.33 | -8.56 | 5% | 38% |
| **B971** | | | | | | | |
| LanL2DZ | -164.30 | -170.92 | -21.96 | -30.98 | -9.02 | 5% | 41% |
| def2-SVP | -170.17 | -179.88 | -23.15 | -32.86 | -9.71 | 6% | 42% |
| def2-TZVP | -165.64 | -175.78 | -22.20 | -32.34 | -10.14 | 6% | 46% |
| def-QZVP | -164.48 | -174.63 | -22.52 | -32.67 | -10.15 | 6% | 45% |
| **BP86** | | | | | | | |
| LanL2DZ | -170.32 | -183.17 | -27.50 | -40.35 | -12.85 | 7% | 47% |
| def2-SVP | -176.24 | -189.00 | -30.00 | -42.76 | -12.76 | 7% | 42% |
| def2-TZVP | -170.68 | -183.71 | -28.95 | -41.98 | -13.03 | 8% | 45% |
| def-QZVP | -169.77 | -182.61 | -29.51 | -42.35 | -12.84 | 8% | 43% |
| **M06** | | | | | | | |
| LanL2DZ | -165.62 | -175.98 | -21.46 | -31.82 | -10.36 | 6% | 48% |
| def2-SVP | -169.66 | -180.13 | -21.56 | -32.03 | -10.47 | 6% | 49% |
| def2-TZVP | -165.77 | -176.18 | -21.42 | -31.83 | -10.41 | 6% | 49% |
| def-QZVP | -165.57 | -174.70 | -22.22 | -31.35 | -9.13 | 5% | 41% |
| **M06L** | | | | | | | |
| LanL2DZ | -163.43 | -178.62 | -21.25 | -36.44 | -15.19 | 9% | 71% |
| def2-SVP | -165.93 | -182.34 | -21.29 | -37.70 | -16.41 | 10% | 77% |
| def2-TZVP | -165.01 | -181.33 | -22.23 | -38.55 | -16.32 | 10% | 73% |
| def-QZVP | -164.25 | -179.87 | -22.83 | -38.45 | -15.62 | 9% | 68% |
| **CCSD(T)//MP2** | | | | | | | |
| LanL2DZ | -157.98 | -163.29 | -15.76 | -21.07 | -5.31 | 3% | 34% |
| def2-SVP | -167.74 | -178.99 | -14.26 | -25.51 | -11.25 | 7% | 79% |
| def2-TZVP | -164.35 | -168.76 | -21.59 | -26.00 | -4.41 | 3% | 20% |
| def-QZVP | - | - | - | - | - | - | - |

[a] See ref. 26 of the paper. ($\Delta IE_{coop} = \Delta IE_{A-B} = \Delta IE_{B-C}$)

[b] $\%\Delta IE_{A-B} = \frac{|\Delta IE_{coop}|}{IE_{A-B}^{ABC}} \times 100$, $\%\Delta IE_{B-C} = \frac{|\Delta IE_{coop}|}{IE_{B-C}^{ABC}} \times 100$

**Table S3**. Calculated values for interaction energies (IE, kcal/mol) between the defined fragments frozen in the optimized geometry of the complexes studied here, and related, $\Delta IE_{coop}$[a], $\%\Delta IE_{A-B}$ and $\%\Delta IE_{B-C}$ values[b] in [($\eta^5$-Cp)Au(CO)] complex, at 24 levels of theory.

| Methods | $IE_{A-B}^{ABC}$ | $IE_{A-BC}^{ABC}$ | $IE_{B-C}^{ABC}$ | $IE_{AB-C}^{ABC}$ | $\Delta IE_{coop}$ | $\%\Delta IE_{A-B}$ | $\%\Delta IE_{B-C}$ |
|---|---|---|---|---|---|---|---|
| **B3LYP** | | | | | | | |
| LanL2DZ | -169.53 | -185.31 | -44.45 | -60.23 | -15.78 | 9% | 35% |
| def2-SVP | -175.83 | -192.78 | -43.51 | -60.46 | -16.95 | 10% | 39% |
| def2-TZVP | -173.82 | -192.79 | -42.54 | -61.51 | -18.97 | 11% | 44% |
| def-QZVP | -172.40 | -190.65 | -44.02 | -62.27 | -18.25 | 11% | 41% |
| **B971** | | | | | | | |
| LanL2DZ | -171.44 | -188.65 | -45.20 | -62.41 | -17.21 | 10% | 38% |
| def2-SVP | -177.27 | -196.13 | -44.24 | -63.10 | -18.86 | 11% | 43% |
| def2-TZVP | -177.17 | -197.61 | -44.17 | -64.61 | -20.44 | 11% | 46% |
| def-QZVP | -175.72 | -195.52 | -45.65 | -65.45 | -19.80 | 11% | 43% |
| **BP86** | | | | | | | |
| LanL2DZ | -181.08 | -194.79 | -57.88 | -71.59 | -13.71 | 7% | 24% |
| def2-SVP | -187.08 | -201.23 | -57.89 | -72.04 | -14.15 | 8% | 24% |
| def2-TZVP | -185.17 | -201.38 | -56.78 | -72.99 | -16.21 | 9% | 28% |
| def-QZVP | -184.08 | -199.45 | -58.36 | -73.73 | -15.37 | 8% | 26% |
| **M06** | | | | | | | |
| LanL2DZ | -171.47 | -190.23 | -36.97 | -55.73 | -18.76 | 11% | 51% |
| def2-SVP | -177.27 | -197.10 | -36.83 | -56.66 | -19.83 | 11% | 54% |
| def2-TZVP | -176.87 | -197.20 | -37.34 | -57.67 | -20.33 | 11% | 54% |
| def-QZVP | -176.74 | -196.90 | -38.36 | -58.52 | -20.16 | 11% | 52% |
| **M06L** | | | | | | | |
| LanL2DZ | -168.59 | -190.59 | -43.41 | -65.41 | -22.00 | 13% | 51% |
| def2-SVP | -174.29 | -196.39 | -44.56 | -66.66 | -22.10 | 13% | 50% |
| def2-TZVP | -175.71 | -198.67 | -46.08 | -69.04 | -22.96 | 13% | 50% |
| def-QZVP | -175.60 | -198.64 | -47.00 | -70.04 | -23.04 | 13% | 49% |
| **CCSD(T)//MP2** | | | | | | | |
| LanL2DZ | -163.17 | -185.91 | -27.11 | -49.85 | -22.74 | 14% | 84% |
| def2-SVP | -179.46 | -200.89 | -38.95 | -60.38 | -21.43 | 12% | 55% |
| def2-TZVP | -183.78 | -205.83 | -43.72 | -65.77 | -22.05 | 12% | 50% |
| def-QZVP | - | - | - | - | - | - | - |

[a] See ref. 26 of the paper. ($\Delta IE_{coop} = \Delta IE_{A-B} = \Delta IE_{B-C}$)

[b] $\%\Delta IE_{A-B} = \frac{|\Delta IE_{coop}|}{IE_{A-B}^{ABC}} \times 100$, $\%\Delta IE_{B-C} = \frac{|\Delta IE_{coop}|}{IE_{B-C}^{ABC}} \times 100$

**Table S4.** Bond dissociation energies, cooperative energies[a] (all in kcal/mol) and the percentages of changes in the bond dissociation energies of A–B and B–C bonds[b] in [($\eta^5$-Cp)Cu(CO)] complex, at 24 levels of theory.

| Methods | $-BDE_{A-B}$ | $-BDE_{A-BC}$ | $-BDE_{B-C}$ | $-BDE_{AB-C}$ | $E_{coop}$ | $\%\Delta BDE_{A-B}$ | $\%\Delta BDE_{B-C}$ |
|---|---|---|---|---|---|---|---|
| **B3LYP** | | | | | | | |
| LanL2DZ | -187.86 | -192.88 | -39.95 | -44.97 | -5.02 | 3% | 13% |
| def2-SVP | -189.71 | -197.94 | -39.02 | -47.25 | -8.23 | 4% | 21% |
| def2-TZVP | -186.65 | -192.27 | -37.33 | -42.95 | -5.62 | 3% | 15% |
| def2-QZVP | -185.02 | -190.13 | -37.49 | -42.60 | -5.11 | 3% | 14% |
| **B971** | | | | | | | |
| LanL2DZ | -188.28 | -194.20 | -38.59 | -44.51 | -5.92 | 3% | 15% |
| def2-SVP | -189.83 | -199.35 | -37.46 | -46.98 | -9.52 | 5% | 25% |
| def2-TZVP | -188.54 | -195.16 | -36.74 | -43.36 | -6.62 | 3% | 18% |
| def2-QZVP | -186.81 | -193.02 | -36.85 | -43.06 | -6.21 | 3% | 17% |
| **BP86** | | | | | | | |
| LanL2DZ | -195.30 | -202.95 | -47.33 | -54.98 | -7.65 | 4% | 16% |
| def2-SVP | -198.42 | -210.42 | -47.03 | -59.03 | -12.00 | 6% | 25% |
| def2-TZVP | -197.45 | -205.78 | -46.72 | -55.05 | -8.33 | 4% | 18% |
| def2-QZVP | -195.91 | -203.56 | -46.93 | -54.58 | -7.65 | 4% | 16% |
| **M06** | | | | | | | |
| LanL2DZ | -193.55 | -198.49 | -41.26 | -46.20 | -4.94 | 3% | 12% |
| def2-SVP | -195.46 | -204.09 | -38.78 | -47.41 | -8.63 | 4% | 22% |
| def2-TZVP | -194.82 | -200.88 | -39.11 | -45.17 | -6.06 | 3% | 15% |
| def2-QZVP | -192.27 | -198.61 | -38.31 | -44.65 | -6.34 | 3% | 16% |
| **M06L** | | | | | | | |
| LanL2DZ | -195.47 | -202.92 | -47.08 | -54.53 | -7.45 | 4% | 16% |
| def2-SVP | -194.85 | -209.04 | -42.04 | -56.23 | -14.19 | 7% | 34% |
| def2-TZVP | -198.91 | -208.17 | -45.66 | -54.92 | -9.26 | 5% | 20% |
| def2-QZVP | -195.86 | -207.00 | -43.53 | -54.67 | -11.14 | 6% | 26% |
| **CCSD(T)//MP2** | | | | | | | |
| LanL2DZ | -178.60 | -185.76 | -30.20 | -37.36 | -7.16 | 4% | 24% |
| def2-SVP | -182.11 | -192.02 | -28.15 | -38.06 | -9.91 | 5% | 35% |
| def2-TZVP | -185.25 | -194.32 | -30.27 | -39.34 | -9.07 | 5% | 30% |
| def2-QZVP | - | - | - | - | - | - | - |

[a] See ref. 26 of the paper. ($E_{coop} = \Delta BDE_{A-B} = \Delta BDE_{B-C}$).

[b] $\%\Delta BDE_{A-B} = \frac{|E_{coop}|}{BDE_{A-B}} \times 100$, $\%\Delta BDE_{B-C} = \frac{|E_{coop}|}{BDE_{B-C}} \times 100$

**Table S5.** Bond dissociation energies, cooperative energies[a] (all in kcal/mol) and the percentages of changes in the bond dissociation energies of A–B and B–C bonds[b] in [(η$^5$-Cp)Ag(CO)] complex, at 24 levels of theory.

| Methods | $-BDE_{A-B}$ | $-BDE_{A-BC}$ | $-BDE_{B-C}$ | $-BDE_{AB-C}$ | $E_{coop}$ | $\%\Delta BDE_{A-B}$ | $\%\Delta BDE_{B-C}$ |
|---|---|---|---|---|---|---|---|
| **B3LYP** | | | | | | | |
| LanL2DZ | -164.24 | -168.90 | -26.05 | -30.71 | -4.66 | 3% | 18% |
| def2-SVP | -169.76 | -174.22 | -27.43 | -31.89 | -4.46 | 3% | 16% |
| def2-TZVP | -163.68 | -168.64 | -25.79 | -30.75 | -4.96 | 3% | 19% |
| def-QZVP | -162.64 | -167.42 | -26.23 | -31.01 | -4.78 | 3% | 18% |
| **B971** | | | | | | | |
| LanL2DZ | -172.68 | -169.84 | -25.41 | -22.57 | 2.84 | 2% | 11% |
| def2-SVP | -169.88 | -175.62 | -26.80 | -32.54 | -5.74 | 3% | 21% |
| def2-TZVP | -165.45 | -171.65 | -25.85 | -32.05 | -6.20 | 4% | 24% |
| def2-QZVP | -164.35 | -170.45 | -26.23 | -32.33 | -6.10 | 4% | 23% |
| **BP86** | | | | | | | |
| LanL2DZ | -169.93 | -179.62 | -30.42 | -40.11 | -9.69 | 6% | 32% |
| def2-SVP | -176.01 | -185.37 | -32.94 | -42.30 | -9.36 | 5% | 28% |
| def2-TZVP | -170.56 | -180.27 | -31.82 | -41.53 | -9.71 | 6% | 30% |
| def2-QZVP | -169.68 | -179.13 | -32.40 | -41.85 | -9.45 | 6% | 29% |
| **M06** | | | | | | | |
| LanL2DZ | -165.14 | -172.24 | -24.51 | -31.61 | -7.10 | 4% | 29% |
| def2-SVP | -169.39 | 176.14 | -24.97 | -31.72 | -6.75 | 4% | 27% |
| def2-TZVP | -165.55 | -172.48 | -24.64 | -31.57 | -6.93 | 4% | 28% |
| def2-QZVP | -165.40 | -170.86 | -25.59 | -31.05 | -5.46 | 3% | 21% |
| **M06L** | | | | | | | |
| LanL2DZ | -168.82 | -174.45 | -24.71 | -30.34 | -5.63 | 3% | 23% |
| def2-SVP | -170.86 | -177.69 | -25.30 | -32.13 | -6.83 | 4% | 27% |
| def2-TZVP | -164.84 | -177.00 | -25.99 | -38.15 | -12.16 | 7% | 47% |
| def2-QZVP | -164.20 | -175.41 | -26.74 | -37.95 | -11.21 | 7% | 42% |
| **CCSD(T)//MP2** | | | | | | | |
| LanL2DZ | -157.48 | -158.57 | -19.67 | -20.76 | -1.09 | <1% | 6% |
| def2-SVP | -167.85 | -176.53 | -21.26 | -29.94 | -8.68 | 5% | 41% |
| def2-TZVP | -164.35 | -168.76 | -21.59 | -26.00 | -4.41 | 3% | 20% |
| def2-QZVP | - | - | - | - | - | - | - |

[a] See ref. 26 of the paper. ($E_{coop} = \Delta BDE_{A-B} = \Delta BDE_{B-C}$).

[b] $\%\Delta BDE_{A-B} = \frac{|E_{coop}|}{BDE_{A-B}} \times 100$, $\%\Delta BDE_{B-C} = \frac{|E_{coop}|}{BDE_{B-C}} \times 100$

**Table S6.** Bond dissociation energies, cooperative energies[a] (all in kcal/mol) and the percentages of changes in the bond dissociation energies of A–B and B–C bonds[b] in [(η$^5$-Cp)Au(CO)] complex, at 24 levels of theory.

| Methods | $-BDE_{A-B}$ | $-BDE_{A-BC}$ | $-BDE_{B-C}$ | $-BDE_{AB-C}$ | $E_{coop}$ | $\%\Delta BDE_{A-B}$ | $\%\Delta BDE_{B-C}$ |
|---|---|---|---|---|---|---|---|
| **B3LYP** | | | | | | | |
| LanL2DZ | -172.76 | -182.43 | -48.79 | -58.46 | -9.67 | 6% | 20% |
| def2-SVP | -177.14 | -187.05 | -47.98 | -57.89 | -9.91 | 6% | 21% |
| def2-TZVP | -174.57 | -186.77 | -46.95 | -59.15 | -12.20 | 7% | 26% |
| def-QZVP | -173.13 | -184.90 | -48.15 | -59.92 | -11.77 | 7% | 24% |
| **B971** | | | | | | | |
| LanL2DZ | -174.90 | -186.19 | -49.31 | -60.60 | -11.29 | 6% | 23% |
| def2-SVP | -178.77 | -190.92 | -48.45 | -60.60 | -12.15 | 7% | 25% |
| def2-TZVP | -180.47 | -194.72 | -48.97 | -63.22 | -14.25 | 8% | 29% |
| def-QZVP | -176.60 | -190.31 | -49.50 | -63.21 | -13.71 | 8% | 28% |
| **BP86** | | | | | | | |
| LanL2DZ | -184.66 | -194.51 | -60.48 | -70.33 | -9.85 | 5% | 16% |
| def2-SVP | -188.79 | -198.24 | -60.60 | -70.05 | -9.45 | 5% | 16% |
| def2-TZVP | -186.31 | -198.04 | -59.47 | -71.20 | -11.73 | 6% | 20% |
| def-QZVP | -185.17 | -196.34 | -60.77 | -71.94 | -11.17 | 6% | 18% |
| **M06** | | | | | | | |
| LanL2DZ | -173.91 | -185.60 | -45.52 | -54.21 | -11.69 | 7% | 26% |
| def2-SVP | -177.84 | -190.00 | -42.32 | -54.48 | -12.16 | 7% | 29% |
| def2-TZVP | -176.80 | -189.69 | -42.74 | -55.63 | -12.89 | 7% | 30% |
| def-QZVP | -176.66 | -189.58 | -43.56 | -56.48 | -12.92 | 7% | 30% |
| **M06L** | | | | | | | |
| LanL2DZ | -171.04 | -188.19 | -47.00 | -64.15 | -17.15 | 10% | 36% |
| def2-SVP | -174.84 | -191.20 | -48.35 | -64.71 | -16.36 | 9% | 34% |
| def2-TZVP | -175.73 | -193.36 | -49.63 | -67.26 | -17.63 | 10% | 35% |
| def-QZVP | -175.61 | -193.56 | -50.33 | -68.28 | -17.95 | 10% | 36% |
| **CCSD(T)//MP2** | | | | | | | |
| LanL2DZ | -168.80 | -182.44 | -33.74 | -47.38 | -13.64 | 8% | 40% |
| def2-SVP | -181.02 | -195.83 | -43.38 | -58.19 | -14.81 | 8% | 34% |
| def2-TZVP | -185.25 | -194.32 | -30.27 | -39.34 | -9.07 | 5% | 30% |
| def-QZVP | - | - | - | - | - | - | - |

[a] See ref. 26 of the paper. ($E_{coop} = \Delta BDE_{A-B} = \Delta BDE_{B-C}$).

[b] $\%\Delta BDE_{A-B} = \frac{|E_{coop}|}{BDE_{A-B}} \times 100$, $\%\Delta BDE_{B-C} = \frac{|E_{coop}|}{BDE_{B-C}} \times 100$

**Table S7.** Computed structural parameters (Å) in [($\eta^5$-Cp)M(CO)$_n$] complexes at the M06L/def2-TZVP level of theory.

| Complex | Dyad | | | Triad | | |
|---|---|---|---|---|---|---|
| | **M…Cp[a]** | **M−CO[b]** | **C=O[c]** | **M…Cp** | **M−CO** | **C=O** |
| [($\eta^5$-Cp)Cu(CO)] | 1.763 | 1.854 | 1.119 | 1.800 | 1.765 | 1.142 |
| [($\eta^5$-Cp)Ag(CO)] | 2.147 | 2.152 | 1.117 | 2.112 | 1.949 | 1.138 |
| [($\eta^5$-Cp)Au(CO)][d] | 2.035 | 1.885 | 1.129 | 2.014 | 1.804 | 1.155 |
| [($\eta^5$-Cp)Co(CO)$_2$] | 1.584 | 1.746 | 1.130 | 1.688 | 1.738 | 1.150 |
| [($\eta^5$-Cp)Rh(CO)$_2$] | 1.780 | 1.826 | 1.131 | 1.938 | 1.856 | 1.148 |
| [($\eta^5$-Cp)Ir(CO)$_2$] | 2.042 | 1.825 | 1.139 | 1.967 | 1.860 | 1.157 |
| [($\eta^5$-Cp)Mn(CO)$_3$][d] | 1.546 | 1.822 | 1.134 | 1.767 | 1.796 | 1.151 |
| [($\eta^5$-Cp)Tc(CO)$_3$] | 1.681 | 1.880 | 1.138 | 1.972 | 1.910 | 1.152 |
| [($\eta^5$-Cp)Re(CO)$_3$] | 1.689 | 1.891 | 1.140 | 1.978 | 1.926 | 1.154 |
| [($\eta^5$-Cp)V(CO)$_4$] | 1.805 | 1.955 | 1.137 | 1.914 | 1.946 | 1.150 |
| [($\eta^5$-Cp)Nb(CO)$_4$] | 1.941 | 2.072 | 1.138 | 2.107 | 2.103 | 1.149 |
| [($\eta^5$-Cp)Ta(CO)$_4$] | 1.950 | 2.065 | 1.140 | 2.110 | 2.103 | 1.515 |

[a]Distance from the center of the ring on Cp ligand coordinated to metal ion.

[b]Average bond length of M–CO

[c]Average bond length of C=O

[d] M06L//MP2/def2-TZVP

Bond length for a free CO ligand is equal to 1.128 Å, at M06L/def2-TZVP level of theory.

** Cartesian coordinates of the optimized structures, at M06L/def2-TZVP level of theory.

**[($\eta^5$-Cp)Cu(CO)]**

| | | | |
|---|---|---|---|
| 29 | -0.374215000 | 0.000000000 | 0.001154000 |
| 8 | -3.281482000 | 0.000338000 | -0.000545000 |
| 6 | -2.139438000 | 0.000668000 | 0.000870000 |
| 6 | 1.424214000 | 0.583242000 | -1.057061000 |
| 6 | 1.423404000 | -0.824593000 | -0.882125000 |
| 6 | 1.425386000 | -1.093024000 | 0.510662000 |
| 6 | 1.427683000 | 0.148748000 | 1.196135000 |
| 6 | 1.426842000 | 1.184643000 | 0.227440000 |
| 1 | 1.432521000 | 1.104551000 | -2.000925000 |
| 1 | 1.431289000 | -1.561401000 | -1.669422000 |
| 1 | 1.435202000 | -2.069304000 | 0.968251000 |
| 1 | 1.439255000 | 0.281916000 | 2.266037000 |
| 1 | 1.437263000 | 2.243441000 | 0.431424000 |

**[($\eta^5$-Cp)Ag(CO)]**

| | | | |
|---|---|---|---|
| 47 | -0.392312000 | -0.000885000 | 0.000542000 |
| 8 | -3.479077000 | 0.001234000 | -0.000743000 |
| 6 | -2.341239000 | -0.000338000 | 0.000433000 |
| 6 | 1.719297000 | 0.711918000 | 0.972515000 |
| 6 | 1.717611000 | 1.146439000 | -0.375965000 |
| 6 | 1.718446000 | -0.002129000 | -1.205790000 |
| 6 | 1.720373000 | -1.146437000 | -0.370066000 |
| 6 | 1.721622000 | -0.704986000 | 0.976149000 |
| 1 | 1.746483000 | 1.347743000 | 1.843462000 |
| 1 | 1.743936000 | 2.171179000 | -0.711724000 |
| 1 | 1.744708000 | -0.004662000 | -2.284211000 |
| 1 | 1.748687000 | -2.172875000 | -0.700892000 |
| 1 | 1.750798000 | -1.336452000 | 1.850201000 |

**[($\eta^5$-Cp)Au(CO)]**

| | | | |
|---|---|---|---|
| 79 | 0.281534000 | -0.000431000 | -0.000734000 |
| 8 | 3.241263000 | 0.001552000 | 0.002643000 |
| 6 | 2.085831000 | 0.000893000 | 0.001717000 |
| 6 | -1.731603000 | -1.205413000 | 0.130565000 |
| 6 | -1.730884000 | -0.495574000 | -1.106046000 |
| 6 | -1.731730000 | 0.899823000 | -0.812943000 |
| 6 | -1.733029000 | 1.052212000 | 0.604583000 |
| 6 | -1.732978000 | -0.248724000 | 1.187642000 |
| 1 | -1.744418000 | -2.279620000 | 0.246119000 |
| 1 | -1.743486000 | -0.937438000 | -2.091960000 |
| 1 | -1.744547000 | 1.700927000 | -1.537861000 |
| 1 | -1.746253000 | 1.989205000 | 1.142473000 |
| 1 | -1.746232000 | -0.470771000 | 2.244983000 |

**[($\eta^5$-Cp)Co(CO)$_2$]**

| | | | |
|---|---|---|---|
| 27 | -0.138549000 | -0.001765000 | 0.000125000 |
| 8 | -2.157153000 | -2.065311000 | -0.000492000 |
| 8 | -2.127507000 | 2.092758000 | -0.000473000 |
| 6 | -1.355337000 | -1.241197000 | 0.000243000 |
| 6 | -1.337072000 | 1.258036000 | 0.000270000 |
| 6 | 1.555390000 | 0.956775000 | -0.719401000 |
| 6 | 1.560600000 | -0.376190000 | -1.163090000 |
| 6 | 1.515301000 | -1.201977000 | 0.000412000 |
| 6 | 1.560680000 | -0.375488000 | 1.163394000 |
| 6 | 1.555401000 | 0.957218000 | 0.718867000 |
| 1 | 1.544417000 | 1.836077000 | -1.343034000 |
| 1 | 1.560672000 | -0.714595000 | -2.185698000 |
| 1 | 1.477903000 | -2.280095000 | 0.000741000 |
| 1 | 1.560869000 | -0.713255000 | 2.186209000 |
| 1 | 1.544469000 | 1.836902000 | 1.341965000 |

**[($\eta^5$-Cp)Rh(CO)$_2$]**

| | | | |
|---|---|---|---|
| 45 | -0.162211000 | 0.000049000 | 0.003642000 |
| 8 | -2.315582000 | -2.093420000 | -0.007340000 |
| 8 | -2.308866000 | 2.104511000 | -0.007637000 |
| 6 | -1.492011000 | -1.292595000 | -0.006246000 |
| 6 | -1.487173000 | 1.302125000 | -0.004584000 |
| 6 | 1.798544000 | 0.824538000 | -0.877138000 |
| 6 | 1.798247000 | -0.559370000 | -1.079687000 |
| 6 | 1.728354000 | -1.180367000 | 0.210233000 |
| 6 | 1.789477000 | -0.172785000 | 1.210571000 |
| 6 | 1.762368000 | 1.066396000 | 0.539450000 |
| 1 | 1.813927000 | 1.583147000 | -1.643094000 |
| 1 | 1.809876000 | -1.070377000 | -2.028274000 |
| 1 | 1.719634000 | -2.244190000 | 0.390043000 |
| 1 | 1.795545000 | -0.326642000 | 2.276412000 |
| 1 | 1.769267000 | 2.039500000 | 1.005246000 |

**[($\eta^5$-Cp)Ir(CO)$_2$]**

| | | | |
|---|---|---|---|
| 77 | -0.133270000 | -0.001111000 | 0.002936000 |
| 8 | -2.283206000 | -2.116469000 | -0.009893000 |
| 8 | -2.262608000 | 2.139851000 | -0.009841000 |
| 6 | -1.469602000 | -1.292906000 | -0.008371000 |
| 6 | -1.458608000 | 1.307440000 | -0.007421000 |
| 6 | 1.860675000 | 0.835422000 | -0.872407000 |
| 6 | 1.857842000 | -0.558102000 | -1.086068000 |
| 6 | 1.787599000 | -1.190942000 | 0.202101000 |
| 6 | 1.837523000 | -0.183296000 | 1.214061000 |
| 6 | 1.822485000 | 1.069372000 | 0.546727000 |
| 1 | 1.877785000 | 1.603543000 | -1.643464000 |
| 1 | 1.869813000 | -1.063837000 | -2.049416000 |
| 1 | 1.781364000 | -2.265893000 | 0.377243000 |
| 1 | 1.840665000 | -0.344401000 | 2.289652000 |
| 1 | 1.831212000 | 2.047167000 | 1.026065000 |

**[($\eta^5$-Cp)Mn(CO)$_3$]**

| | | | |
|---|---|---|---|
| 25 | -0.049013000 | 0.000096000 | -0.000602000 |
| 8 | -1.665183000 | -1.800735000 | -1.682122000 |
| 8 | -1.635204000 | 2.373234000 | -0.731052000 |
| 8 | -1.695617000 | -0.544790000 | 2.381894000 |
| 6 | -1.049478000 | -1.088964000 | -1.019487000 |
| 6 | -1.033070000 | 1.436077000 | -0.441227000 |
| 6 | -1.067521000 | -0.327607000 | 1.442363000 |
| 6 | 1.719161000 | 1.063773000 | 0.566505000 |
| 6 | 1.728923000 | 0.842739000 | -0.841037000 |
| 6 | 1.723398000 | -0.549091000 | -1.065635000 |
| 6 | 1.707741000 | -1.204884000 | 0.197036000 |
| 6 | 1.711527000 | -0.201269000 | 1.196806000 |
| 1 | 1.721056000 | 2.021729000 | 1.060030000 |
| 1 | 1.727321000 | 1.606628000 | -1.601725000 |
| 1 | 1.712130000 | -1.034098000 | -2.028454000 |
| 1 | 1.703369000 | -2.269280000 | 0.362440000 |
| 1 | 1.685404000 | -0.373694000 | 2.261047000 |

**[($\eta^5$-Cp)Tc(CO)$_3$]**

| | | | |
|---|---|---|---|
| 43 | -0.058234000 | -0.000001000 | 0.000247000 |
| 8 | -1.805694000 | -1.783357000 | -1.771699000 |
| 8 | -1.794361000 | 2.432968000 | -0.662257000 |
| 8 | -1.818900000 | -0.640819000 | 2.421590000 |
| 6 | -1.173999000 | -1.099224000 | -1.093075000 |
| 6 | -1.168199000 | 1.500220000 | -0.406249000 |
| 6 | -1.183504000 | -0.393653000 | 1.492872000 |
| 6 | 1.912870000 | 1.051043000 | 0.597038000 |
| 6 | 1.915926000 | 0.879476000 | -0.818298000 |
| 6 | 1.914592000 | -0.504741000 | -1.091616000 |
| 6 | 1.911529000 | -1.205365000 | 0.148088000 |
| 6 | 1.911665000 | -0.236721000 | 1.182895000 |
| 1 | 1.933302000 | 1.990867000 | 1.124179000 |
| 1 | 1.923341000 | 1.669788000 | -1.551611000 |
| 1 | 1.916535000 | -0.956009000 | -2.070924000 |
| 1 | 1.933296000 | -2.274882000 | 0.275822000 |
| 1 | 1.903963000 | -0.446244000 | 2.240893000 |

**[($\eta^5$-Cp)Re(CO)$_3$]**

| | | | |
|---|---|---|---|
| 75 | -0.043076000 | -0.000320000 | -0.000003000 |
| 8 | -1.803147000 | -2.168460000 | -1.297500000 |
| 8 | -1.798663000 | 2.209343000 | -1.231315000 |
| 8 | -1.817631000 | -0.036714000 | 2.516323000 |
| 6 | -1.174964000 | -1.337678000 | -0.800149000 |
| 6 | -1.172113000 | 1.362389000 | -0.759942000 |
| 6 | -1.184948000 | -0.022998000 | 1.551079000 |
| 6 | 1.935013000 | 1.167857000 | 0.325903000 |
| 6 | 1.937888000 | 0.657963000 | -1.008154000 |
| 6 | 1.937177000 | -0.752694000 | -0.938342000 |
| 6 | 1.934651000 | -1.134091000 | 0.436049000 |
| 6 | 1.930079000 | 0.058142000 | 1.206679000 |
| 1 | 1.955989000 | 2.207015000 | 0.609847000 |
| 1 | 1.948802000 | 1.247278000 | -1.910531000 |
| 1 | 1.942214000 | -1.426341000 | -1.779944000 |
| 1 | 1.959865000 | -2.141039000 | 0.818068000 |
| 1 | 1.922624000 | 0.110389000 | 2.283999000 |

**[($\eta^5$-Cp)V(CO)$_4$]**

| | | | |
|---|---|---|---|
| 23 | 0.042144000 | -0.000315000 | 0.000135000 |
| 6 | 1.902881000 | 1.104021000 | -0.563442000 |
| 6 | 1.940840000 | -0.160689000 | -1.200443000 |
| 6 | 2.000257000 | -1.152507000 | -0.197774000 |
| 6 | -0.896343000 | -1.629236000 | -0.510573000 |
| 6 | -0.938979000 | 0.500611000 | -1.601982000 |
| 8 | -1.443812000 | -2.593130000 | -0.816369000 |
| 8 | -1.509617000 | 0.801885000 | -2.554170000 |
| 1 | 1.870464000 | 2.061884000 | -1.055805000 |
| 1 | 1.933877000 | -0.336387000 | -2.263618000 |
| 1 | 2.033169000 | -2.217236000 | -0.363252000 |
| 6 | 1.937000000 | 0.885640000 | 0.836068000 |
| 6 | 1.998944000 | -0.509080000 | 1.056181000 |
| 1 | 2.030482000 | -0.998069000 | 2.016677000 |
| 6 | -0.901063000 | -0.531573000 | 1.620182000 |
| 8 | -1.452263000 | -0.844305000 | 2.579694000 |
| 6 | -0.942503000 | 1.593067000 | 0.521236000 |
| 8 | -1.515512000 | 2.541669000 | 0.829159000 |
| 1 | 1.926112000 | 1.646582000 | 1.599650000 |

| $[(\eta^5\text{-Cp})Nb(CO)_4]$ | | | | $[(\eta^5\text{-Cp})Ta(CO)_4]$ | | | |
|---|---|---|---|---|---|---|---|
| 41 | -0.058569000 | -0.000627000 | 0.000395000 | 73 | -0.049281000 | 0.000820000 | 0.000086000 |
| 8 | 1.647496000 | -2.146894000 | 1.751686000 | 8 | 1.650429000 | -1.940075000 | 1.984577000 |
| 8 | 1.631387000 | 1.749825000 | 2.161385000 | 8 | 1.659741000 | 1.971558000 | 1.945799000 |
| 8 | 1.674307000 | -1.733075000 | -2.135046000 | 8 | 1.679979000 | -1.975118000 | -1.918444000 |
| 6 | 1.053682000 | -1.383634000 | 1.130796000 | 6 | 1.062298000 | -1.248118000 | 1.277622000 |
| 6 | 1.043447000 | 1.127739000 | 1.394662000 | 6 | 1.068298000 | 1.268964000 | 1.252178000 |
| 6 | 1.070475000 | -1.117787000 | -1.374838000 | 6 | 1.081537000 | -1.269354000 | -1.233873000 |
| 6 | -2.164690000 | 1.152491000 | -0.342938000 | 6 | -2.138221000 | 1.166717000 | -0.336345000 |
| 6 | -2.204147000 | 0.660665000 | 0.980611000 | 6 | -2.186924000 | 0.664818000 | 0.986116000 |
| 6 | -2.189887000 | -0.749065000 | 0.926984000 | 6 | -2.197390000 | -0.744823000 | 0.921259000 |
| 6 | -2.141248000 | -1.136819000 | -0.432412000 | 6 | -2.153944000 | -1.123546000 | -0.439506000 |
| 6 | -2.126252000 | 0.041545000 | -1.221928000 | 6 | -2.118283000 | 0.058336000 | -1.222964000 |
| 1 | -2.178639000 | 2.191428000 | -0.632414000 | 1 | -2.143007000 | 2.207288000 | -0.619413000 |
| 1 | -2.238363000 | 1.259002000 | 1.877730000 | 1 | -2.213640000 | 1.256341000 | 1.887816000 |
| 1 | -2.216466000 | -1.414640000 | 1.775518000 | 1 | -2.228655000 | -1.416672000 | 1.764629000 |
| 1 | -2.144319000 | -2.149491000 | -0.802878000 | 1 | -2.165139000 | -2.134196000 | -0.815422000 |
| 1 | -2.122014000 | 0.084373000 | -2.299262000 | 1 | -2.113806000 | 0.105853000 | -2.300129000 |
| 6 | 1.060211000 | 1.386456000 | -1.114239000 | 6 | 1.087480000 | 1.238345000 | -1.259910000 |
| 8 | 1.658257000 | 2.150827000 | -1.729908000 | 8 | 1.688932000 | 1.925319000 | -1.960829000 |