

## Supporting information

Monomer geometries for:

### Cl-Au-PH3

|    |           |           |           |
|----|-----------|-----------|-----------|
| Au | 0.000000  | 0.000000  | 0.000000  |
| Cl | 0.000000  | 0.000000  | 2.300000  |
| P  | 0.000000  | 0.000000  | -2.273000 |
| H  | 1.254483  | 0.000000  | -2.923262 |
| H  | -0.627242 | -1.086414 | -2.923262 |
| H  | -0.627242 | 1.086414  | -2.923262 |

### Cl-Au-(NHC-H)

|    |           |           |           |
|----|-----------|-----------|-----------|
| C  | 0.000000  | 0.000000  | 0.000000  |
| N  | 0.000000  | 0.000000  | 1.364054  |
| C  | 1.281943  | 0.000000  | 1.893768  |
| C  | 2.131063  | 0.000000  | 0.829446  |
| N  | 1.330139  | 0.000000  | -0.302453 |
| Au | -1.546985 | 0.000000  | -1.232336 |
| Cl | -3.330493 | -0.000000 | -2.647144 |
| H  | 1.661820  | 0.000000  | -1.260454 |
| H  | 3.212573  | 0.000000  | 0.786367  |
| H  | 1.479606  | 0.000000  | 2.957881  |
| H  | -0.859452 | 0.000000  | 1.901538  |

### Cl-Au-(C-PH<sub>3</sub>)<sub>2</sub>

|    |           |           |           |
|----|-----------|-----------|-----------|
| C  | 0.000000  | 0.000000  | 0.000000  |
| P  | 0.000000  | 0.000000  | 1.674219  |
| Au | 1.809183  | 0.000000  | -0.938873 |
| Cl | 3.838184  | 0.000000  | -1.991821 |
| P  | -1.368971 | 0.000000  | -0.963807 |
| H  | -1.282487 | 0.000000  | 2.296076  |
| H  | 0.648186  | -1.086265 | 2.327112  |
| H  | 0.648186  | 1.086265  | 2.327112  |
| H  | -2.615745 | 0.000000  | -0.273136 |
| H  | -1.529682 | 1.086266  | -1.869671 |
| H  | -1.529682 | -1.086266 | -1.869671 |

Dimer geometry for Cl-Au-(NHC-B)

|    |            |           |           |
|----|------------|-----------|-----------|
| Au | -3.748000  | -0.934000 | 18.583000 |
| Cl | -2.677422  | -2.062171 | 20.339606 |
| O  | -1.462525  | 0.858341  | 16.112124 |
| N  | -5.483204  | -0.557109 | 16.102095 |
| N  | -4.219002  | 1.160753  | 16.462113 |
| N  | -1.118825  | 1.865961  | 18.165450 |
| C  | -4.560423  | -0.056549 | 16.979328 |
| C  | -4.896160  | 1.411329  | 15.280624 |
| H  | -4.750348  | 2.331964  | 14.708869 |
| C  | -5.702888  | 0.328648  | 15.051206 |
| H  | -6.429380  | 0.123385  | 14.260312 |
| C  | -6.278813  | -1.765279 | 16.314942 |
| H  | -5.906576  | -2.215662 | 17.259532 |
| H  | -6.070585  | -2.491459 | 15.501597 |
| C  | -7.764413  | -1.450908 | 16.392390 |
| C  | -8.209691  | -0.241280 | 16.967260 |
| H  | -7.483610  | 0.474972  | 17.386615 |
| C  | -9.581554  | 0.051342  | 17.018571 |
| H  | -9.912065  | 0.998482  | 17.471140 |
| C  | -10.522894 | -0.862674 | 16.514864 |
| H  | -11.598737 | -0.631623 | 16.558996 |
| C  | -10.085631 | -2.078039 | 15.960785 |
| H  | -10.815914 | -2.801847 | 15.567512 |
| C  | -8.711605  | -2.366666 | 15.892479 |
| H  | -8.372076  | -3.312398 | 15.439305 |
| C  | -3.298418  | 2.068940  | 17.119042 |
| H  | -3.680099  | 2.254183  | 18.145031 |
| H  | -3.314134  | 3.033131  | 16.574481 |
| C  | -1.858940  | 1.506433  | 17.078368 |
| C  | 0.276958   | 1.436448  | 18.437444 |
| C  | 0.286403   | -0.082126 | 18.705184 |
| H  | -0.391643  | -0.346231 | 19.540455 |
| H  | 1.309650   | -0.428169 | 18.956300 |
| H  | -0.062974  | -0.626392 | 17.806110 |
| C  | 0.734293   | 2.227700  | 19.674625 |
| H  | 0.747066   | 3.317409  | 19.465108 |
| H  | 1.753672   | 1.917943  | 19.973378 |
| H  | 0.073980   | 2.040560  | 20.545536 |
| C  | 1.182038   | 1.789489  | 17.240068 |
| H  | 0.865739   | 1.243418  | 16.332889 |
| H  | 2.230603   | 1.517914  | 17.477674 |
| H  | 1.143182   | 2.877722  | 17.027721 |
| H  | -1.642347  | 2.209627  | 18.974624 |

|    |            |           |           |
|----|------------|-----------|-----------|
| Au | -5.164000  | 0.934000  | 20.768000 |
| Cl | -6.234785  | 2.061849  | 19.011353 |
| O  | -7.449157  | -0.857659 | 23.239642 |
| N  | -3.428432  | 0.557720  | 23.248642 |
| N  | -4.692706  | -1.160240 | 22.889332 |
| N  | -7.793051  | -1.865716 | 21.186551 |
| C  | -4.351346  | 0.056911  | 22.371704 |
| C  | -4.015345  | -1.410486 | 24.070770 |
| H  | -4.161073  | -2.330955 | 24.642815 |
| C  | -3.208565  | -0.327747 | 24.299737 |
| H  | -2.481944  | -0.122261 | 25.090452 |
| C  | -2.632869  | 1.765856  | 23.035337 |
| H  | -3.005302  | 2.216098  | 22.090755 |
| H  | -2.840905  | 2.492162  | 23.848620 |
| C  | -1.147311  | 1.451536  | 22.957542 |
| C  | -0.702116  | 0.242006  | 22.382450 |
| H  | -1.428237  | -0.474156 | 21.963132 |
| C  | 0.669731   | -0.050567 | 22.330831 |
| H  | 1.000166   | -0.997584 | 21.878107 |
| C  | 1.611116   | 0.863399  | 22.834507 |
| H  | 2.686939   | 0.632408  | 22.790154 |
| C  | 1.173930   | 2.078677  | 23.388744 |
| H  | 1.904244   | 2.802497  | 23.781902 |
| C  | -0.200072  | 2.367270  | 23.457295 |
| H  | -0.539534  | 3.312971  | 23.910562 |
| C  | -5.613426  | -2.068606 | 22.232833 |
| H  | -5.231882  | -2.254215 | 21.206848 |
| H  | -5.597677  | -3.032611 | 22.777722 |
| C  | -7.052881  | -1.506041 | 22.273536 |
| C  | -9.188784  | -1.436140 | 20.914411 |
| C  | -9.198077  | 0.082453  | 20.646604 |
| H  | -8.519869  | 0.346475  | 19.811459 |
| H  | -10.221257 | 0.428595  | 20.395328 |
| H  | -8.848790  | 0.626709  | 21.545719 |
| C  | -9.645946  | -2.227474 | 19.677221 |
| H  | -9.658867  | -3.317165 | 19.886828 |
| H  | -10.665242 | -1.917633 | 19.378203 |
| H  | -8.985413  | -2.040487 | 18.806491 |
| C  | -10.094076 | -1.789058 | 22.111671 |
| H  | -9.777881  | -1.242972 | 23.018876 |
| H  | -11.142583 | -1.517409 | 21.873890 |
| H  | -10.055339 | -2.877286 | 22.324066 |
| H  | -7.269526  | -2.209519 | 20.377437 |

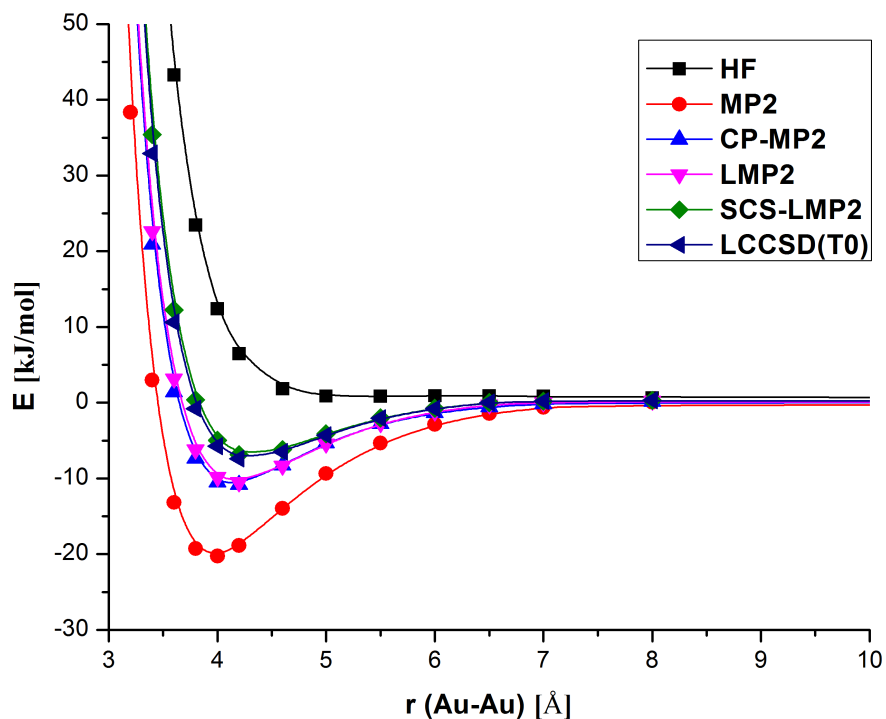


Figure 1: Potential energy curves of the Cl-Au-(C-PH<sub>3</sub>)<sub>2</sub> dimer. All results have been computed with the def2-TZVP basis.

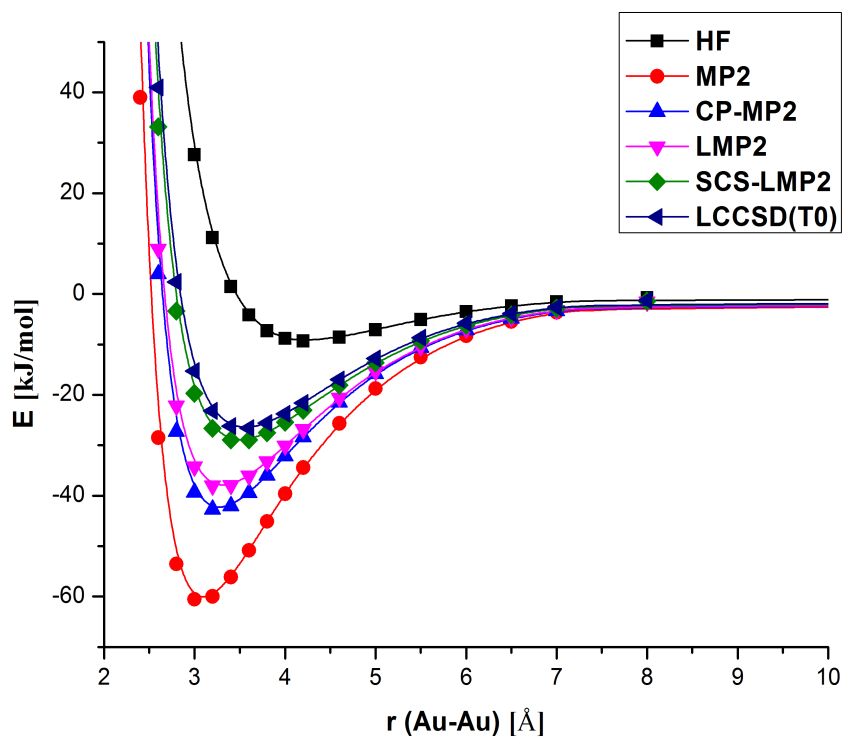


Figure 2: Potential energy curves of the Cl-Au-(NHC-H) dimer (edge-to-edge). All results have been computed with the def2-TZVP basis.

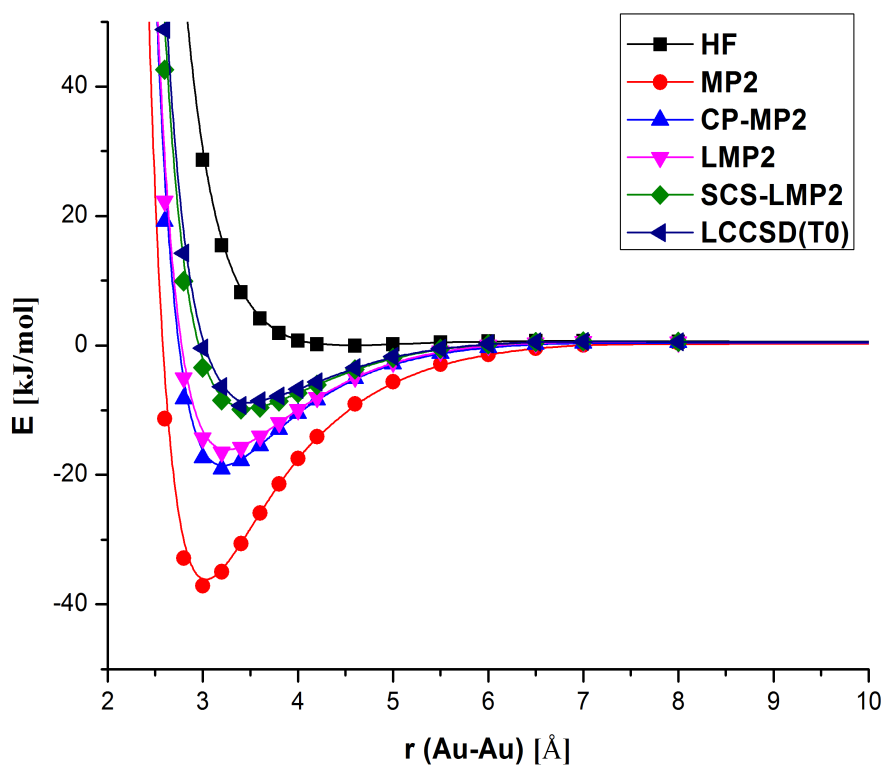


Figure 3: Potential energy curves of the Cl-Au-(NHC-H) dimer (face-to-face). All results have been computed with the def2-TZVP basis.

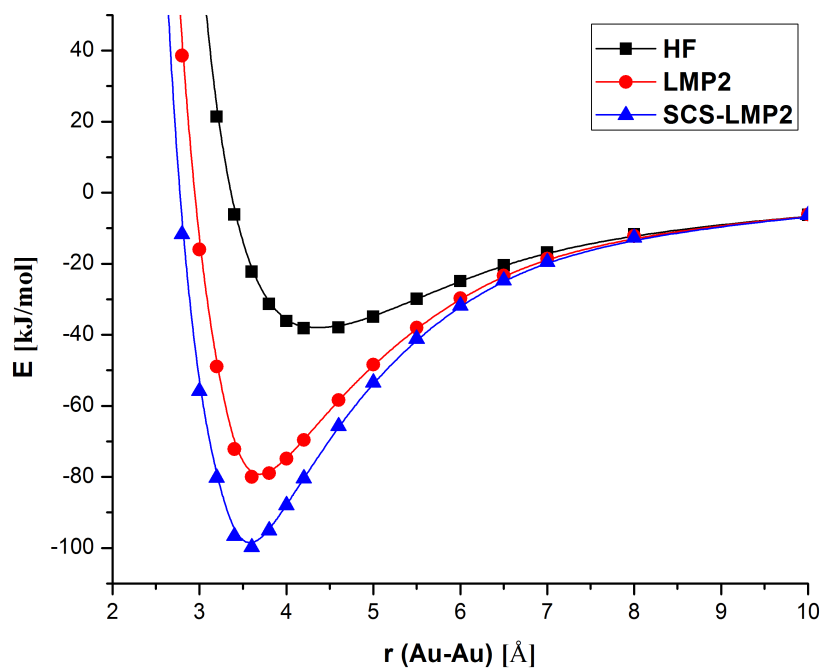


Figure 4: Potential energy curves of the Cl-Au-(NHC-B) dimer. All results have been computed with the def2-TZVP basis.