Supporting Information

From Large 12-Membered Macrometallacycles to Ionic $(NHC)_2M^+Cl^-$ (M = Au, Ag) Type Complexes of Gold and Silver by Modulation of *N*-substituent of Amido-functionalized N-heterocyclic Carbene (NHC) Ligands

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The density functional theory calculations were performed on the eight gold and silver complexes of N-heterocyclic carbenes, namely, the ionic the ionic, [1-(R)-3-{N-(t-butylacetamido)imidazol-2-ylidene}]$_2$M$^+$Cl$^-$, (R = *t*-Bu, *i*-Pr; M = Au, Ag; **1b**, **1c**, **2b**, **2c**) complexes, and the 12-membered macrometallacylic [1-(R)-3-{N-(2,6-di-*i*-propylphenylacetamido)imidazol-2-ylidene}]$_2$M$_2$**,** (R = *t*-Bu, *i*-Pr; M = Au, Ag; **3b**, **3c**, **4b**, **4c**) complexes using GAUSSIAN 03[1] suite of quantum chemical programs.

Input Coordinates for Charge Decomposition Analysis of **1b**, **1c**, **2b**, **2c**, **3b**, **3c**, **4b** and **4d**:

Table S1. Standard Orientation of **1b.**

N	4.304	6.633	3.301
N	4.457	4.763	2.295
N	7.114	2.991	0.787
O	5.861	4.61	-0.165
C	5.176	5.677	2.977
C	3.05	6.335	2.823
H	2.283	6.85	2.923
C	3.145	5.162	2.188
H	2.458	4.705	1.758
C	4.64	7.854	4.072
H	5.568	7.633	4.293
C	4.885	8.972	3.227
H	4.07	9.228	2.79
H	5.543	8.738	2.568
H	5.209	9.707	3.755
C	4.128	7.88	5.347
H	4.35	8.717	5.763
H	4.504	7.16	5.859
H	3.174	7.785	5.311
C	4.999	3.518	1.772
H	4.28	2.988	1.394
H	5.397	3.01	2.496
C	6.05	3.776	0.702

C	8.294	2.99	-0.114
C	8.963	4.332	-0.033
H	8.353	5.012	-0.332
H	9.743	4.333	-0.589
H	9.215	4.508	0.876
C	9.227	1.952	0.393
H	9.541	2.202	1.264
H	9.973	1.872	-0.206
H	8.769	1.11	0.448
C	7.898	2.747	-1.53
H	7.424	1.913	-1.591
H	8.683	2.71	-2.08
H	7.33	3.459	-1.83
H	7.119	2.441	1.342
C	9.291	5.677	3.668
N	10.163	6.633	3.344
N	10.01	4.763	4.35
N	7.353	2.991	5.859
O	8.606	4.61	6.81
C	11.417	6.335	3.822
H	12.184	6.85	3.723
C	11.323	5.162	4.458
H	12.01	4.705	4.887
C	9.827	7.854	2.573
H	8.899	7.633	2.353
C	9.582	8.972	3.418
H	10.397	9.228	3.856
H	8.925	8.738	4.078
H	9.258	9.707	2.891
C	10.339	7.88	1.299
H	10.117	8.717	0.883
H	9.963	7.16	0.787
H	11.293	7.785	1.334
C	9.468	3.518	4.874
H	10.188	2.988	5.251
H	9.07	3.01	4.149
C	8.418	3.776	5.944
C	6.173	2.99	6.76
C	5.505	4.332	6.679
H	6.114	5.012	6.978
H	4.724	4.333	7.234
H	5.252	4.508	5.77
C	5.24	1.952	6.252
H	4.926	2.202	5.382
H	4.494	1.872	6.852
H	5.698	1.11	6.198

C	6.569	2.747	8.175
H	7.043	1.913	8.236
H	5.784	2.71	8.726
H	7.137	3.459	8.476
H	7.348	2.441	5.303
Ag	7.234	5.614	3.323

Table S2. Standard Orientation of **1c**.

O	12.741	3.085	6.471
N	11.171	1.046	9.9
N	11.334	2.923	8.899
N	13.97	4.749	7.389
C	12.05	1.998	9.592
C	9.913	1.365	9.437
H	9.143	0.856	9.539
C	10.012	2.539	8.813
H	9.322	3.009	8.4
C	11.51	-0.182	10.681
H	12.443	0.006	10.914
C	11.68	-1.334	9.826
H	11.938	-2.092	10.357
H	12.36	-1.152	9.175
H	10.852	-1.524	9.377
C	10.928	-0.208	11.957
H	9.972	-0.193	11.873
H	11.218	0.56	12.456
H	11.197	-1.007	12.416
C	11.867	4.172	8.398
H	12.254	4.674	9.131
H	11.146	4.702	8.021
C	12.924	3.936	7.335
C	15.157	4.735	6.506
C	15.849	3.394	6.641
H	16.17	3.289	7.54
H	16.588	3.352	6.031
H	15.226	2.692	6.44
C	14.767	4.956	5.081
H	14.175	4.256	4.799
H	15.553	4.951	4.529
H	14.323	5.803	4.998
C	16.044	5.834	6.982
H	15.599	6.677	6.862
H	16.86	5.828	6.476
H	16.241	5.706	7.912

H	14.087	5.291	8.007
O	15.33	3.085	13.382
N	16.9	1.046	9.953
N	16.737	2.923	10.954
N	14.101	4.749	12.464
C	16.021	1.998	10.261
C	18.158	1.365	10.416
H	18.928	0.856	10.314
C	18.059	2.539	11.04
H	18.749	3.009	11.452
C	16.561	-0.182	9.172
H	15.628	0.006	8.939
C	16.391	-1.334	10.027
H	16.133	-2.092	9.496
H	15.71	-1.152	10.678
H	17.219	-1.524	10.476
C	17.143	-0.208	7.896
H	18.099	-0.193	7.98
H	16.853	0.56	7.397
H	16.874	-1.007	7.437
C	16.204	4.172	11.455
H	15.816	4.674	10.722
H	16.925	4.702	11.832
C	15.147	3.936	12.518
C	12.913	4.735	13.346
C	12.222	3.394	13.211
H	11.901	3.289	12.313
H	11.482	3.352	13.822
H	12.845	2.692	13.413
C	13.304	4.956	14.772
H	13.896	4.256	15.054
H	12.518	4.951	15.324
H	13.748	5.803	14.855
C	12.027	5.834	12.871
H	12.472	6.677	12.99
H	11.211	5.828	13.377
H	11.829	5.706	11.941
H	13.984	5.291	11.846
Au	14.035	2.03	9.926

Table S3. Standard Orientation of **2b**.

O	-2.126	4.866	6.026
N	-3.594	7.031	9.605
N	-3.38	5.157	8.591

N	-0.712	3.406	7.057
H	-0.611	2.96	7.797
C	-2.676	6.094	9.267
C	-4.843	6.69	9.107
H	-5.635	7.188	9.193
C	-4.703	5.512	8.478
H	-5.379	5.024	8.045
C	-2.816	3.906	8.099
H	-3.543	3.324	7.792
H	-2.356	3.45	8.835
C	-1.828	4.124	6.951
C	0.38	3.279	6.061
C	-0.04	2.803	4.757
H	-0.394	1.905	4.838
H	0.721	2.799	4.154
H	-0.727	3.39	4.404
C	1.488	2.48	6.767
H	1.201	1.558	6.877
H	1.665	2.869	7.638
H	2.295	2.504	6.231
C	0.982	4.734	5.935
H	0.364	5.298	5.442
H	1.829	4.695	5.465
H	1.121	5.106	6.821
C	-3.348	8.308	10.366
C	-4.507	8.56	11.307
H	-5.314	8.717	10.791
H	-4.316	9.338	11.853
H	-4.633	7.787	11.878
C	-3.229	9.426	9.375
H	-4.047	9.488	8.857
H	-2.482	9.252	8.78
H	-3.08	10.26	9.846
C	-2.105	8.197	11.232
H	-1.318	8.166	10.666
H	-2.154	7.386	11.763
H	-2.052	8.966	11.821
C	1.498	6.094	9.52
O	0.948	4.866	12.761
N	2.416	7.031	9.182
N	2.202	5.157	10.196
N	-0.466	3.406	11.73
H	-0.567	2.96	10.99
C	3.665	6.69	9.68
H	4.457	7.188	9.594
C	3.525	5.512	10.309

H	4.201	5.024	10.742
C	1.638	3.906	10.688
H	2.365	3.324	10.995
H	1.178	3.45	9.952
C	0.65	4.124	11.836
C	-1.558	3.279	12.726
C	-1.138	2.803	14.03
H	-0.784	1.905	13.949
H	-1.899	2.799	14.633
H	-0.451	3.39	14.383
C	-2.666	2.48	12.02
H	-2.379	1.558	11.91
H	-2.843	2.869	11.149
H	-3.473	2.504	12.556
C	-2.16	4.734	12.852
H	-1.542	5.298	13.345
H	-3.007	4.695	13.323
H	-2.299	5.106	11.966
C	2.17	8.308	8.421
C	3.329	8.56	7.48
H	4.136	8.717	7.996
H	3.138	9.338	6.934
H	3.455	7.787	6.909
C	2.051	9.426	9.412
H	2.869	9.488	9.93
H	1.304	9.252	10.007
H	1.901	10.26	8.941
C	0.927	8.197	7.555
H	0.14	8.166	8.121
H	0.976	7.386	7.024
H	0.874	8.966	6.966
Ag	-0.589	6.06	9.394

Table S4. Standard Orientation of **2c**.

O	5.818	4.908	-0.226
N	4.301	7.095	3.334
N	4.546	5.217	2.32
N	7.192	3.412	0.798
H	7.266	2.945	1.516
C	5.221	6.188	2.975
C	3.061	6.697	2.846
H	2.263	7.167	2.934
C	3.215	5.541	2.243
H	2.548	5.037	1.838

C	4.506	8.383	4.096
C	3.255	8.744	4.855
H	3.434	9.495	5.426
H	2.975	7.995	5.386
H	2.559	8.972	4.233
C	4.861	9.439	3.125
H	5.64	9.171	2.631
H	5.045	10.255	3.595
H	4.129	9.575	2.52
C	5.585	8.179	5.14
H	6.431	8.049	4.704
H	5.376	7.407	5.67
H	5.633	8.953	5.705
C	5.116	3.962	1.835
H	4.397	3.386	1.533
H	5.562	3.515	2.572
C	6.111	4.146	0.701
C	8.317	3.287	-0.183
C	7.866	2.37	-1.257
H	7.168	2.793	-1.765
H	7.532	1.561	-0.867
H	8.605	2.168	-1.835
C	9.47	2.666	0.527
H	10.179	2.5	-0.099
H	9.193	1.837	0.923
H	9.783	3.259	1.214
C	8.71	4.578	-0.704
H	9.582	4.511	-1.102
H	8.733	5.219	0.01
H	8.076	4.861	-1.369
C	9.272	6.188	3.281
O	8.676	4.908	6.482
N	10.192	7.095	2.922
N	9.947	5.217	3.936
N	7.301	3.412	5.458
H	7.227	2.945	4.739
C	11.432	6.697	3.409
H	12.23	7.167	3.322
C	11.278	5.541	4.013
H	11.945	5.037	4.418
C	9.987	8.383	2.16
C	11.238	8.744	1.401
H	11.059	9.495	0.83
H	11.518	7.995	0.87
H	11.934	8.972	2.023
C	9.632	9.439	3.13

H	8.853	9.171	3.625
H	9.448	10.255	2.661
H	10.364	9.575	3.736
C	8.908	8.179	1.116
H	8.062	8.049	1.551
H	9.117	7.407	0.586
H	8.86	8.953	0.551
C	9.377	3.962	4.42
H	10.096	3.386	4.723
H	8.931	3.515	3.683
C	8.382	4.146	5.555
C	6.176	3.287	6.439
C	6.627	2.37	7.513
H	7.326	2.793	8.021
H	6.961	1.561	7.123
H	5.888	2.168	8.091
C	5.024	2.666	5.729
H	4.314	2.5	6.355
H	5.301	1.837	5.333
H	4.711	3.259	5.042
C	5.783	4.578	6.96
H	4.912	4.511	7.358
H	5.76	5.219	6.246
H	6.417	4.861	7.625
Au	7.247	6.193	3.128

Table S5. Standard Orientation of **3b**.

Ag	1.712	9.33	0.035
Ag	-1.712	8.391	-0.035
N	0.848	10.108	-2.815
N	2.814	9.3	-2.836
C	1.786	9.578	-2.016
C	1.299	10.174	-4.108
H	0.826	10.502	-4.839
C	2.54	9.681	-4.127
H	3.102	9.609	-4.865
C	4.13	8.733	-2.414
H	4.075	8.544	-1.454
C	5.215	9.796	-2.614
H	6.019	9.522	-2.164
H	4.916	10.633	-2.249
H	5.393	9.903	-3.551
C	4.427	7.452	-3.108
H	3.69	6.848	-2.993
H	5.22	7.062	-2.732

H	4.563	7.618	-4.042
C	-0.495	10.461	-2.395
O	-1.648	9.421	-4.191
N	-1.876	8.446	-2.111
C	-1.441	9.391	-2.985
H	-0.555	10.47	-1.427
H	-0.732	11.342	-2.726
C	-2.483	7.314	-2.718
C	-1.667	6.335	-3.29
C	-0.141	6.468	-3.224
H	0.06	7.399	-2.991
C	0.414	5.598	-2.111
H	0.248	4.675	-2.315
H	1.36	5.744	-2.033
H	-0.013	5.825	-1.282
C	0.525	6.185	-4.555
H	0.238	5.329	-4.882
H	0.279	6.865	-5.187
H	1.478	6.183	-4.443
C	-2.269	5.23	-3.866
H	-1.737	4.563	-4.237
C	-3.628	5.098	-3.905
H	-4.007	4.354	-4.312
C	-4.435	6.052	-3.351
H	-5.358	5.949	-3.396
C	-3.905	7.174	-2.72
C	-4.781	8.221	-2.069
H	-4.24	8.662	-1.38
C	-5.189	9.293	-3.076
H	-5.657	9.997	-2.622
H	-4.404	9.649	-3.5
H	-5.762	8.903	-3.741
C	-5.981	7.611	-1.376
H	-5.712	6.81	-0.918
H	-6.335	8.239	-0.74
H	-6.653	7.4	-2.027
O	1.648	8.301	4.191
N	1.876	9.275	2.111
C	1.441	8.331	2.985
C	0.495	7.26	2.395
H	0.555	7.252	1.427
H	0.732	6.38	2.726
C	2.483	10.408	2.718
C	1.667	11.386	3.29
C	0.141	11.253	3.224
H	-0.06	10.323	2.991

C	-0.414	12.123	2.111
H	-0.248	13.047	2.315
H	-1.36	11.978	2.033
H	0.013	11.896	1.282
C	-0.525	11.537	4.555
H	-0.238	12.393	4.882
H	-0.279	10.856	5.187
H	-1.478	11.538	4.443
C	2.269	12.492	3.866
H	1.737	13.158	4.237
C	3.628	12.623	3.905
H	4.007	13.367	4.312
C	4.435	11.67	3.351
H	5.358	11.772	3.396
C	3.905	10.548	2.72
C	4.781	9.5	2.069
H	4.24	9.059	1.38
C	5.189	8.428	3.076
H	5.657	7.725	2.622
H	4.404	8.072	3.5
H	5.762	8.818	3.741
C	5.981	10.11	1.376
H	5.712	10.911	0.918
H	6.335	9.483	0.74
H	6.653	10.321	2.027
N	-0.848	7.613	2.815
N	-2.814	8.421	2.836
C	-1.786	8.143	2.016
C	-1.299	7.548	4.108
H	-0.826	7.22	4.839
C	-2.54	8.04	4.127
H	-3.102	8.113	4.865
C	-4.13	8.988	2.414
H	-4.075	9.178	1.454
C	-5.215	7.925	2.614
H	-6.019	8.2	2.164
H	-4.916	7.089	2.249
H	-5.393	7.819	3.551
C	-4.427	10.27	3.108
H	-3.69	10.874	2.993
H	-5.22	10.659	2.732
H	-4.563	10.103	4.042

Table S6. Standard Orientation of **3c**

Au	10.528	-1.242	-1.527

Au	11.152	1.242	1.527
O	7.163	0.309	2.458
N	7.54	-1.41	-1.916
N	8.05	-1.257	0.161
N	9.164	1.298	1.982
C	8.594	-1.281	-1.082
C	6.674	-1.362	0.098
H	6.085	-1.357	0.816
C	6.348	-1.471	-1.207
H	5.494	-1.569	-1.562
C	7.63	-1.456	-3.388
H	8.569	-1.337	-3.643
C	7.169	-2.81	-3.886
H	7.755	-3.491	-3.548
H	7.186	-2.821	-4.846
H	6.275	-2.976	-3.579
C	6.822	-0.304	-3.978
H	5.905	-0.383	-3.701
H	6.873	-0.336	-4.935
H	7.18	0.53	-3.664
C	8.799	-1.053	1.412
H	9.751	-1.007	1.23
H	8.638	-1.788	2.023
C	8.31	0.271	2.031
C	8.606	2.573	2.374
C	8.541	2.925	3.724
C	9.077	2.013	4.81
H	9.506	1.249	4.37
C	7.941	1.467	5.681
H	7.329	0.97	5.134
H	7.478	2.197	6.098
H	8.306	0.891	6.358
C	10.105	2.689	5.637
H	10.822	2.989	5.074
H	10.446	2.073	6.289
H	9.711	3.442	6.084
C	7.937	4.137	4.052
H	7.879	4.383	4.948
C	7.428	4.974	3.099
H	7.027	5.775	3.348
C	7.512	4.626	1.776
H	7.156	5.192	1.13
C	8.127	3.431	1.377
C	8.281	3.083	-0.1
H	8.503	2.129	-0.145
C	9.314	3.775	-0.758

H	9.441	3.402	-1.633
H	10.126	3.693	-0.253
H	9.078	4.703	-0.837
C	7.058	3.264	-0.87
H	7.218	3.895	-1.579
H	6.365	3.603	-0.297
H	6.784	2.426	-1.244
N	12.516	-1.298	-1.982
O	14.517	-0.309	-2.458
N	14.14	1.41	1.916
N	13.63	1.257	-0.161
C	13.086	1.281	1.082
C	15.006	1.362	-0.098
H	15.595	1.357	-0.816
C	15.332	1.471	1.207
H	16.186	1.569	1.562
C	14.05	1.456	3.388
H	13.111	1.337	3.643
C	14.511	2.81	3.886
H	13.925	3.491	3.548
H	14.494	2.821	4.846
H	15.405	2.976	3.579
C	14.858	0.304	3.978
H	15.775	0.383	3.701
H	14.807	0.336	4.935
H	14.5	-0.53	3.664
C	12.881	1.053	-1.412
H	11.929	1.007	-1.23
H	13.042	1.788	-2.023
C	13.37	-0.271	-2.031
C	13.074	-2.573	-2.374
C	13.139	-2.925	-3.724
C	12.603	-2.013	-4.81
H	12.174	-1.249	-4.37
C	13.739	-1.467	-5.681
H	14.351	-0.97	-5.134
H	14.202	-2.197	-6.098
H	13.374	-0.891	-6.358
C	11.575	-2.689	-5.637
H	10.858	-2.989	-5.074
H	11.234	-2.073	-6.289
H	11.969	-3.442	-6.084
C	13.743	-4.137	-4.052
H	13.801	-4.383	-4.948
C	14.252	-4.974	-3.099
H	14.653	-5.775	-3.348

C	14.168	-4.626	-1.776
H	14.524	-5.192	-1.13
C	13.553	-3.431	-1.377
C	13.399	-3.083	0.1
H	13.177	-2.129	0.145
C	12.366	-3.775	0.758
H	12.239	-3.402	1.633
H	11.554	-3.693	0.253
H	12.602	-4.703	0.837
C	14.622	-3.264	0.87
H	14.462	-3.895	1.579
H	15.315	-3.603	0.297
H	14.896	-2.426	1.244

Table S7. Standard Orientation of **4b**

Ag	4.187	-2.249	10.112
Ag	1.757	-4.415	12.018
O	4.105	0.058	13.694
N	4.076	-0.768	11.555
C	3.989	-2.274	13.442
H	4.086	-2.928	12.732
H	4.699	-2.417	14.086
C	4.097	-0.874	12.862
C	3.938	0.572	11.036
C	5.053	1.293	10.654
C	6.431	0.711	10.753
H	6.339	-0.261	10.658
C	7.023	0.971	12.13
H	7.247	1.9	12.212
H	7.815	0.44	12.243
H	6.38	0.736	12.802
C	7.375	1.181	9.649
H	6.938	1.097	8.799
H	8.168	0.642	9.658
H	7.608	2.1	9.799
C	4.855	2.587	10.182
H	5.591	3.092	9.923
C	3.611	3.133	10.091
H	3.505	4.005	9.784
C	2.518	2.392	10.452
H	1.668	2.76	10.375
C	2.666	1.102	10.93
C	1.443	0.265	11.271
H	1.781	-0.525	11.742
C	0.749	-0.246	10.072

H	0.1	-0.903	10.333
H	1.39	-0.647	9.478
H	0.309	0.48	9.622
C	0.54	0.943	12.214
H	0.233	1.766	11.826
H	1.01	1.127	13.03
H	-0.212	0.375	12.4
N	2.703	-2.437	14.086
N	0.641	-2.822	14.46
C	1.648	-3.113	13.61
C	2.354	-1.756	15.221
H	2.919	-1.226	15.735
C	1.092	-1.977	15.458
H	0.592	-1.63	16.16
C	-0.736	-3.342	14.363
C	-1.292	-2.993	13.019
H	-0.6	-3.061	12.358
H	-2.003	-3.601	12.802
H	-1.631	-2.095	13.037
C	-1.59	-2.707	15.392
H	-1.404	-1.766	15.425
H	-2.513	-2.844	15.17
H	-1.404	-3.102	16.248
C	-0.776	-4.798	14.522
H	-0.163	-5.061	15.212
H	-1.665	-5.069	14.765
H	-0.528	-5.218	13.697
N	5.302	-3.842	7.67
N	3.241	-4.227	8.044
C	4.296	-3.551	8.52
C	3.59	-4.908	6.909
H	3.025	-5.439	6.396
C	4.852	-4.687	6.672
H	5.352	-5.034	5.971
C	6.68	-3.322	7.768
C	7.236	-3.671	9.111
H	6.544	-3.603	9.773
H	7.947	-3.063	9.328
H	7.575	-4.569	9.093
C	7.533	-3.957	6.739
H	7.348	-4.898	6.706
H	8.457	-3.82	6.96
H	7.347	-3.563	5.882
C	6.72	-1.867	7.608
H	6.106	-1.603	6.918
H	7.609	-1.596	7.365

H	6.472	-1.446	8.434
C	1.955	-4.39	8.688
O	1.839	-6.722	8.437
N	1.867	-5.896	10.575
H	1.858	-3.736	9.399
H	1.245	-4.247	8.044
C	1.846	-5.79	9.268
C	2.006	-7.236	11.094
C	0.891	-7.957	11.477
C	-0.487	-7.375	11.377
H	-0.396	-6.403	11.472
C	-1.079	-7.635	10.001
H	-1.303	-8.564	9.919
H	-1.871	-7.104	9.888
H	-0.437	-7.4	9.328
C	-1.431	-7.845	12.482
H	-0.994	-7.761	13.331
H	-2.225	-7.306	12.473
H	-1.665	-8.764	12.331
C	1.089	-9.251	11.948
H	0.352	-9.756	12.207
C	2.333	-9.797	12.039
H	2.438	-10.669	12.347
C	3.426	-9.056	11.678
H	4.276	-9.424	11.756
C	3.277	-7.766	11.2
C	4.501	-6.93	10.859
H	4.162	-6.139	10.388
C	5.194	-6.418	12.059
H	5.843	-5.761	11.798
H	4.554	-6.017	12.652
H	5.635	-7.144	12.508
C	5.404	-7.607	9.917
H	5.71	-8.43	10.304
H	4.933	-7.791	9.1
H	6.156	-7.039	9.731

Table S8. Standard Orientation of **4c**

Au	1.256	1.107	0.998
Au	-1.256	-1.107	-0.998
N	2.347	-0.486	3.366
N	0.255	-0.869	2.983
C	1.322	-0.184	2.517
C	1.879	-1.344	4.357
H	2.376	-1.688	5.063

C	0.589	-1.583	4.11
H	0.023	-2.129	4.607
C	3.754	0.019	3.265
C	4.313	-0.345	1.9
H	4.273	-1.294	1.778
H	5.226	-0.052	1.838
H	3.794	0.087	1.216
C	3.751	1.531	3.479
H	3.227	1.95	2.793
H	4.651	1.862	3.442
H	3.372	1.732	4.338
C	4.601	-0.627	4.362
H	4.263	-0.366	5.222
H	5.513	-0.339	4.276
H	4.558	-1.583	4.28
C	-1.045	-0.989	2.325
N	-1.182	-2.544	0.439
O	-1.174	-3.344	2.587
C	-1.158	-2.416	1.766
H	-1.759	-0.82	2.961
H	-1.116	-0.342	1.606
C	-1.032	-3.898	-0.048
C	0.257	-4.429	-0.121
C	1.476	-3.597	0.249
H	1.132	-2.774	0.655
C	2.225	-3.176	-0.986
H	2.649	-3.941	-1.381
H	1.611	-2.789	-1.615
H	2.893	-2.527	-0.75
C	2.348	-4.23	1.275
H	2.697	-5.055	0.933
H	3.072	-3.638	1.489
H	1.833	-4.405	2.067
C	0.394	-5.739	-0.558
H	1.244	-6.117	-0.605
C	-0.7	-6.498	-0.922
H	-0.588	-7.379	-1.198
C	-1.957	-5.939	-0.88
H	-2.69	-6.449	-1.141
C	-2.156	-4.627	-0.454
C	-3.526	-4	-0.417
H	-3.422	-3.044	-0.602
C	-4.482	-4.578	-1.467
H	-4.712	-5.479	-1.229
H	-5.278	-4.043	-1.502
H	-4.054	-4.574	-2.325

C	-4.149	-4.142	0.982
H	-3.552	-3.774	1.637
H	-4.984	-3.669	1.008
H	-4.3	-5.069	1.172
N	1.182	2.544	-0.439
O	1.174	3.344	-2.587
C	1.158	2.416	-1.766
C	1.045	0.989	-2.325
H	1.759	0.82	-2.961
H	1.116	0.342	-1.606
C	1.032	3.898	0.048
C	-0.257	4.429	0.121
C	-1.476	3.597	-0.249
H	-1.132	2.774	-0.655
C	-2.225	3.176	0.986
H	-2.649	3.941	1.381
H	-1.611	2.789	1.615
H	-2.893	2.527	0.75
C	-2.348	4.23	-1.275
H	-2.697	5.055	-0.933
H	-3.072	3.638	-1.489
H	-1.833	4.405	-2.067
C	-0.394	5.739	0.558
H	-1.244	6.117	0.605
C	0.7	6.498	0.922
H	0.588	7.379	1.198
C	1.957	5.939	0.88
H	2.69	6.449	1.141
C	2.156	4.627	0.454
C	3.526	4	0.417
H	3.422	3.044	0.602
C	4.482	4.578	1.467
H	4.712	5.479	1.229
H	5.278	4.043	1.502
H	4.054	4.574	2.325
C	4.149	4.142	-0.982
H	3.552	3.774	-1.637
H	4.984	3.669	-1.008
H	4.3	5.069	-1.172
N	-0.255	0.869	-2.983
N	-2.347	0.486	-3.366
C	-1.322	0.184	-2.517
C	-1.879	1.344	-4.357
H	-2.376	1.688	-5.063
C	-0.589	1.583	-4.11
H	-0.023	2.129	-4.607

C	-3.754	-0.019	-3.265
C	-4.313	0.345	-1.9
H	-4.273	1.294	-1.778
H	-5.226	0.052	-1.838
H	-3.794	-0.087	-1.216
C	-3.751	-1.531	-3.479
H	-3.227	-1.95	-2.793
H	-4.651	-1.862	-3.442
H	-3.372	-1.732	-4.338
C	-4.601	0.627	-4.362
H	-4.263	0.366	-5.222
H	-5.513	0.339	-4.276
H	-4.558	1.583	-4.28

Table S9. Mulliken charge analysis data of **1b**, **1c**, **2b** and **2c** complexes and its ligand fragments.

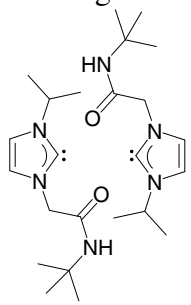
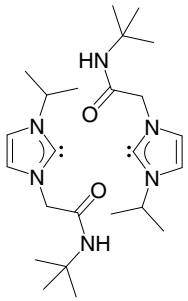
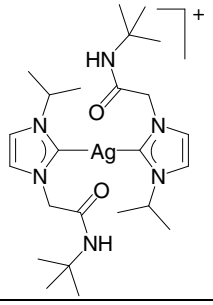
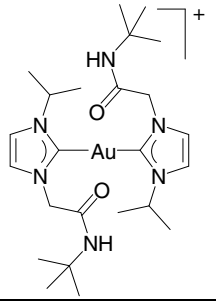
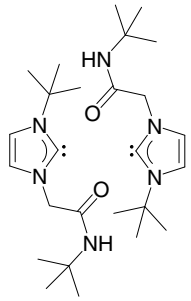
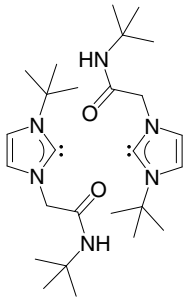
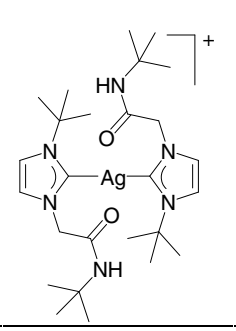
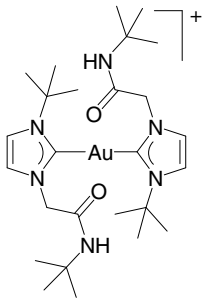
Compd. No.	fragment	$C_{carbene}$	Ag	Compd. No.	Compounds	$C_{carbene}$	Au
	Ag^+		1.00		Au^+		1.00
		0.08 0.08				0.09 0.09	
1b		0.29 0.29	-0.22	**1c**		0.29 0.29	-0.26
	Ag^+		1.00		Au^+		1.00
		0.09 0.09				0.07 0.07	
2b		0.29 0.29	-0.28	**2c**		0.30 0.30	-0.35

Table S10. Mulliken charge analysis data of **3b**, **3c**, **4b** and **4c** complexes and its ligand fragments.

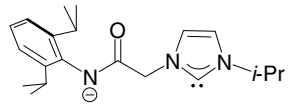
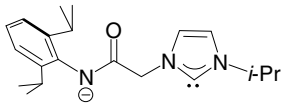
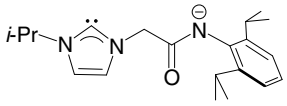
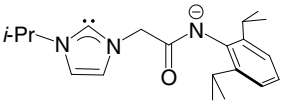
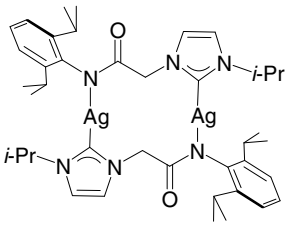
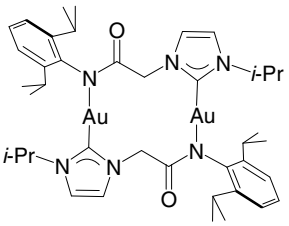
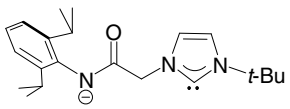
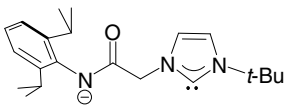
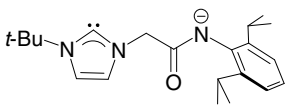
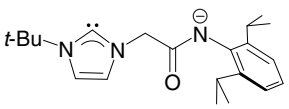
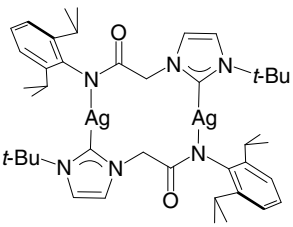
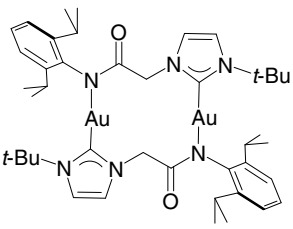
Compd. No.	fragment	$C_{carbene}$	Ag	Compd. No.	Compounds	$C_{carbene}$	Au
	Ag^+		1.00		Au^+		1.00
	Ag^+		1.00		Au^+		1.00
							
		0.07 0.07				0.07 0.07	
3b		0.29 0.29	-0.02 -0.02	**3c**		0.30 0.30	-0.08 -0.08
	Ag^+		1.00		Au^+		1.00
	Ag^+		1.00		Au^+		1.00
							
		0.07 0.07				0.07 0.07	
4b		0.28 0.28	-0.07 -0.07	**4c**		0.30 0.30	-0.13 -0.13

Table S11. Electronic configuration of Ag and Au in **1b**, **1c**, **2b**, and **2c** complexes.

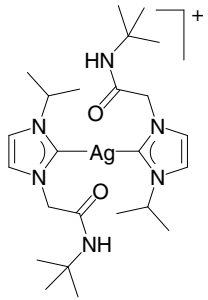
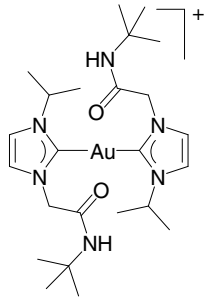
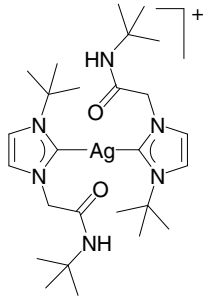
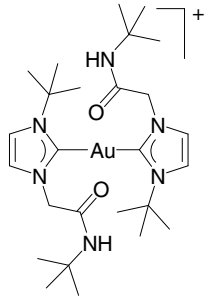
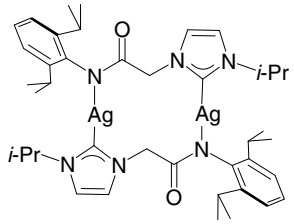
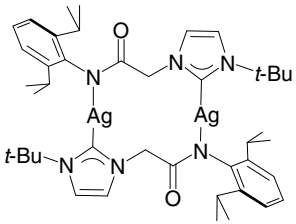
Compd. No.	Ag configuration in fragment	*5s*	*4d*	*5p*	*5d*	*6p*	Compd. No.	Ag configuration in fragment	*6s*	*5d*	*6p*	*6d*	*7p*
	Ag^+		10.00					Au^+		10.00			
1b		0.75	9.78	0	0.01	0.01	**1c**		1.03	9.62	0.01	0.01	0.01
	Ag^+		10.00					Au^+		10.00			
2b		0.71	9.79	0.01	0.01	0	**2c**		1.01	9.63	0.01	0.01	0.01

Table S12. Electronic configuration of Ag and Au in **3b**, **3c**, **4b**, and **4c** complexes.

Compd. No.	Ag configuration in fragment	*5s*	*4d*	*5d*	*6p*	*7p*
	Ag^+	0.01	9.99			
	Ag^+	0.01	9.99			
3b		0.69 0.69	9.78 9.78	0.01 0.01	0.01 0.01	0.01 0.01
	Ag^+	0	9.99			
	Ag^+	0	9.99			
4b		0.69 0.69	9.78 9.78	0.01 0.01	0.01 0.01	0 0

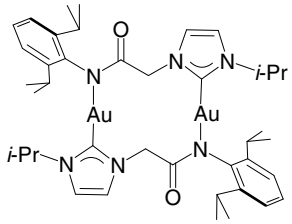
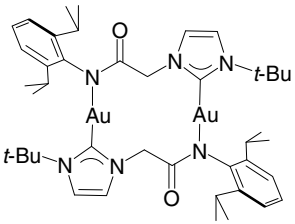
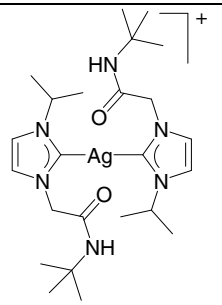
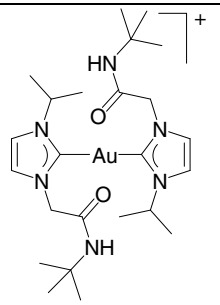
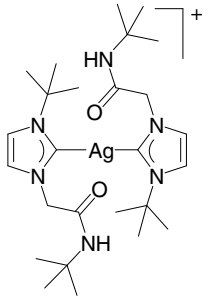
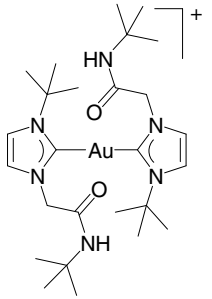
Compd. No.	Au configuration in fragment	*6s*	*5d*	*6p*	*6d*	*7p*
	Au^+	0.01	9.99			
	Au^+	0.01	9.99			
3c		1.00 1.00	9.60 9.60	0.01 0.01	0.01 0.01	0 0
	Au^+	0.01	9.99			
	Au^+	0.01	9.99			
4c		0.99 0.99	9.60 9.60	0 0	0.01 0.01	0.01 0.01

Table S13. NHC—M (M = Ag, Au) bond distance and NHC—M (M = Ag, Au) bond energy in **1b**, **1c**, **2b** and **2c** complexes.

Complex/fragment[a]	*d*/(C_{carb}—M) (M = Ag, Au) (Å)	D_e(NHC—M) (M = Ag, Au) (kcal/mol)	Complex/fragment[a]	*d*/(C_{carb}—M) (M = Ag, Au) (Å)	D_e(NHC—M) (M = Ag, Au) (kcal/mol)
 **1b**	2.087(4)	86.9	 **1c**	2.014(8)	113.6
 **2b**	2.0912(17)	83.2	 **2c**	2.028(5)	112.4

[a] The NHC—M bond energies for the **1b, 1c**, **2b** and **2c** complexes were calculated from their respective cationic fragments as shown in column 1 of the table.

Table S14. NHC—M (M = Ag, Au) bond distance and NHC—M (M = Ag, Au) bond energy in **3b**, **3c**, **4b** and **4c** complexes.

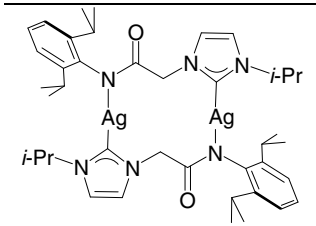
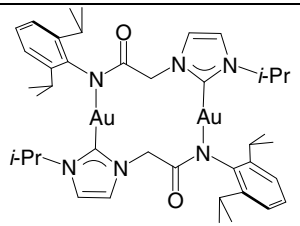
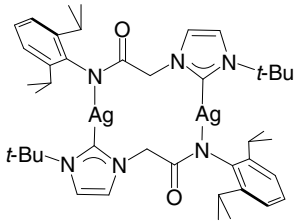
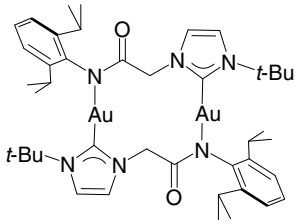
Complex	*d*/(C_{carb}—M) (M = Ag, Au) (Å)	D_e(NHC—M) (M = Ag, Au) (kcal/mol)	Complex	*d*/(C_{carb}—M) (M = Ag, Au) (Å)	D_e(NHC—M) (M = Ag, Au) (kcal/mol)
 **3b**	2.066(8)	62.4	 **3c**	1.982(3)	81.0
 **4b**	2.032(4) 2.045(4)	62.0	 **4c**	1.989(3) 1.990(3)	79.0

Table S15. Charge decomposition analysis (CDA) results showing the $NHC \xrightarrow{\sigma} M$ donation (*d*), the $NHC \xleftarrow{\pi} M$ (*b*) donation (*b*), *d*/*b* ratio and the NHC↔M repulsive polarization (*r*) for the ionic **1b**, **1c**, **2b** and **2c** complexes.

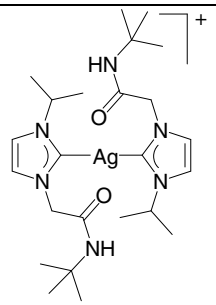
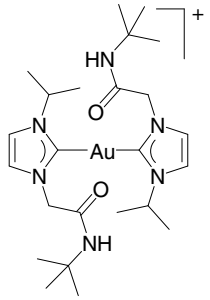
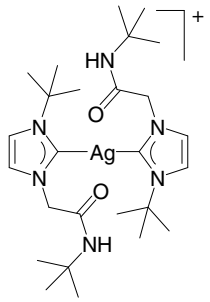
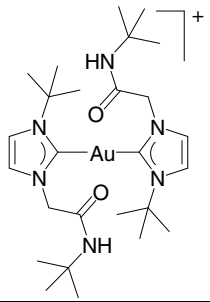
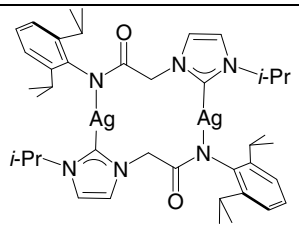
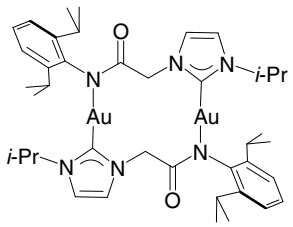
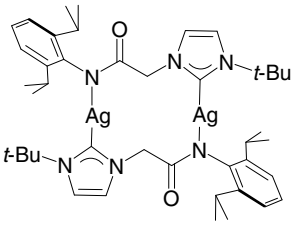
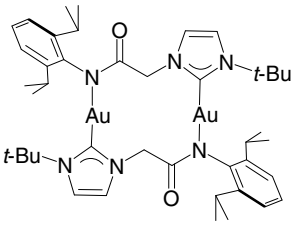
Compd . . No	fragment	$NHC \xrightarrow{\sigma} M$ (*d*)	$NHC \xleftarrow{\pi} M$ (*b*)	*d*/*b* ratio	Repulsive polarization (*r*)
1b		1.316	0.115	11.44	-0.065
1c		1.119	0.214	5.23	-0.072
2b		1.403	0.112	12.53	-0.082
2c		1.228	0.209	5.88	-0.081

Table S16. Charge decomposition analysis (CDA) results showing the $NHC \xrightarrow{\sigma} M$ donation (*d*), the $NHC \xleftarrow{\pi} M$ (*b*) donation (*b*), *d*/*b* ratio and the NHC↔M repulsive polarization (*r*) for the macrometallacyclic **3b**, **3c**, **4b** and **4c** complexes.

Compd. No	fragment	$NHC \xrightarrow{\sigma} M$ (*d*)	$NHC \xleftarrow{\pi} M$ (*b*)	*d*/*b* ratio	Repulsive polarization (*r*)
3b		2.258	0.178	12.68	-0.151
3c		1.886	0.338	5.58	-0.148
4b		2.403	0.195	12.32	-0.165
4c		2.059	0.366	5.63	-0.166

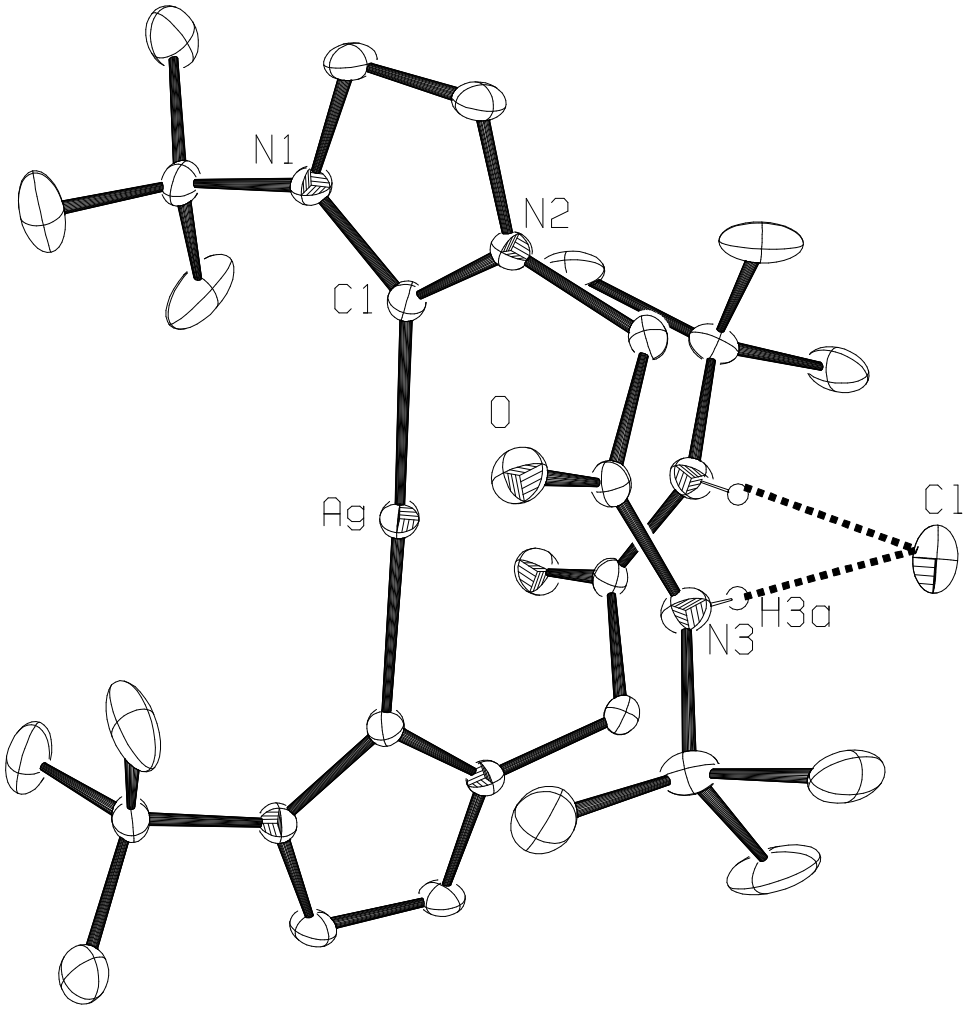


Figure S1. ORTEP of **2b** with thermal ellipsoids drawn at 20 % probability level. Selected bond lengths (Å) and angles (°): N1-C1 1.355(2), N2-C1 1.353(2), Ag-C1 2.0912(17), C1-Ag-C1 178.18(9), N1-C1-N2 104.56(14).

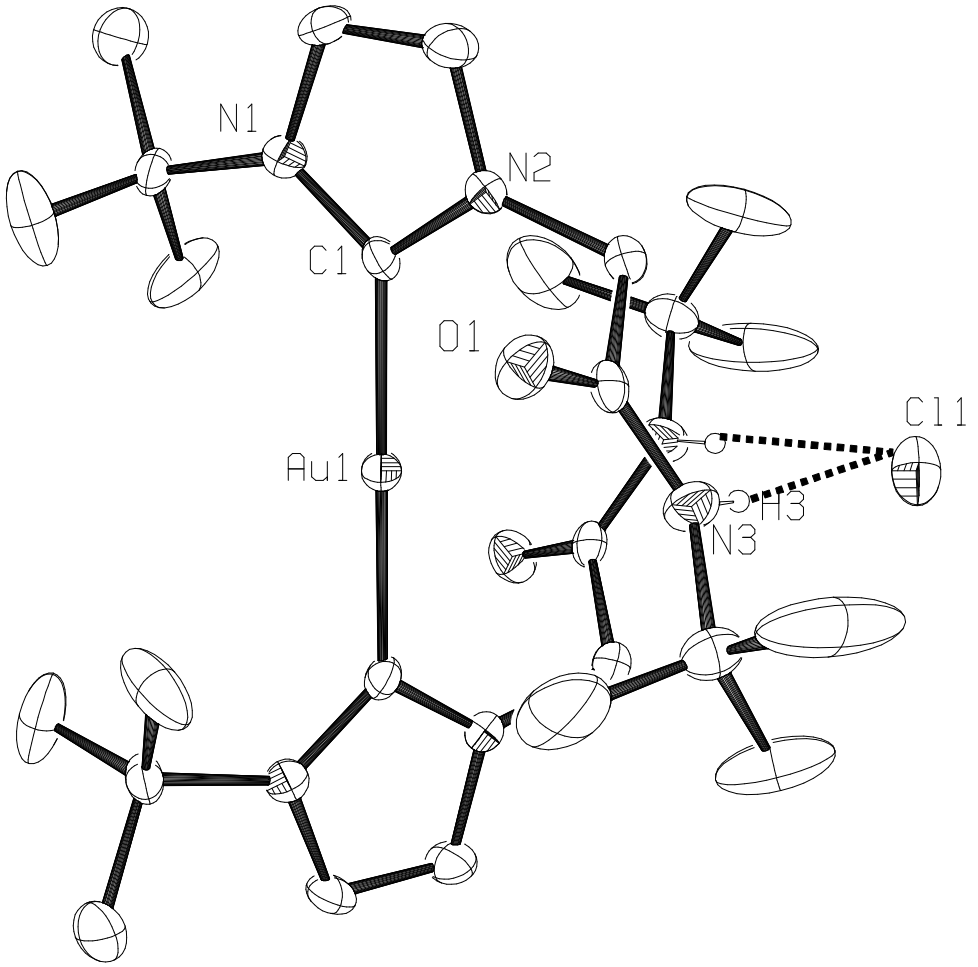


Figure S2. ORTEP of **2c** with thermal ellipsoids drawn at 20 % probability level. Selected bond lengths (Å) and angles (^{o}): N1-C1 1.344(7), N2-C1 1.354(6), Au1-C1 2.028(5), C1-Au1-C1 179.6(3), N1-C1-N2 105.6(4).

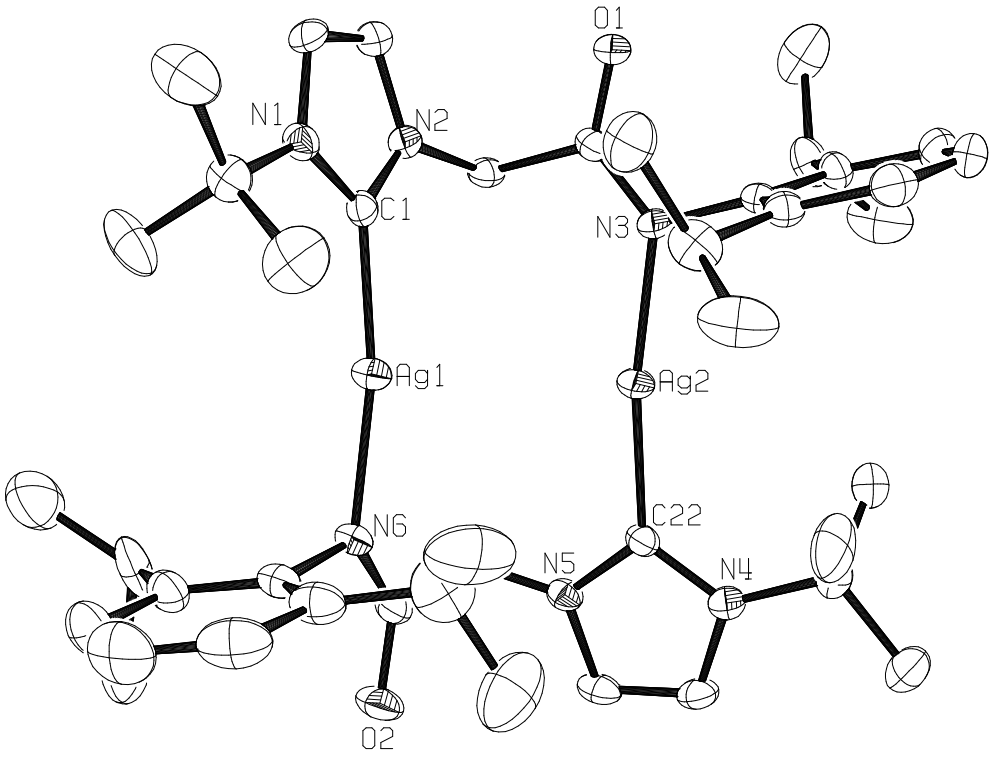


Figure S3. ORTEP of **4b** with thermal ellipsoids drawn at 20 % probability level. Selected bond lengths (Å) and angles (^{o}): Ag1-C1 2.032(4), Ag2-C22 2.045(4), Ag1-N6 2.073(3), Ag2-N3 2.062(3), N1-C1 1.369(4), N2-C1 1.351(4), N4-C22 1.358(4), N5-C22 1.339(4), C1-Ag1-N6 170.31(14), C22-Ag2-N3 170.84(15), N1-C1-N2 102.5(3), N4-C22-N5 104.4(4). The *boat* conformation is shown.

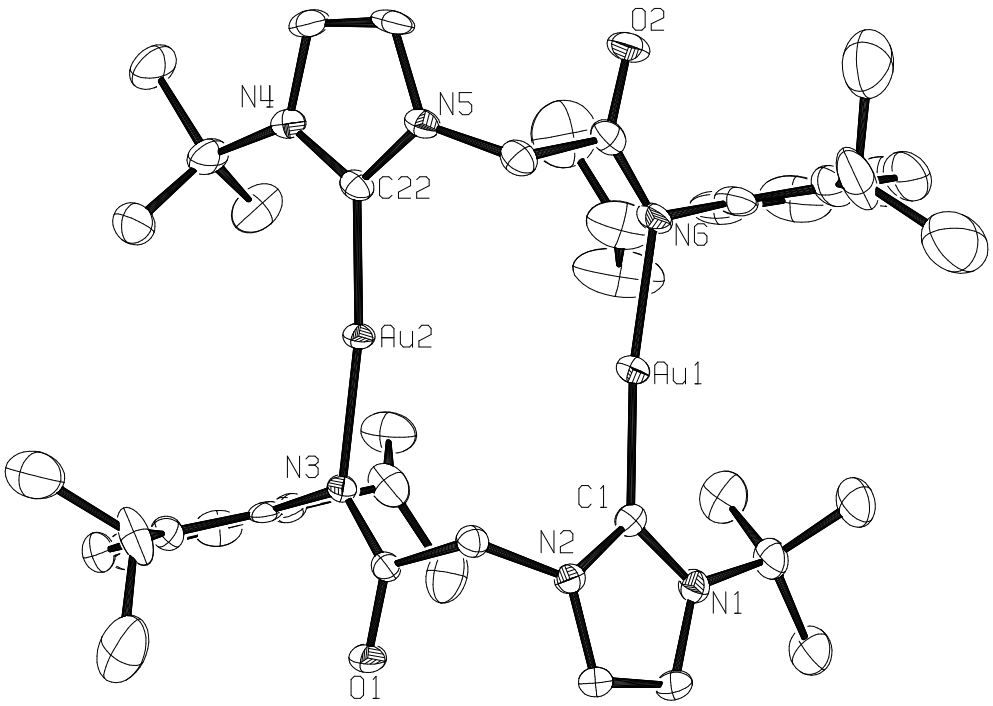


Figure S4. ORTEP of **4c** with thermal ellipsoids drawn at 50 % probability level. Selected bond lengths (Å) and angles (^{o}): N1-C1 1.354(4), N2-C1 1.350(4), Au1-C1 1.989(3), Au1-N6 2.039(3), N4-C22 1.355(4), N5-C22 1.342(4), Au2-C22 1.990(3), Au2-N3 2.030(3), C1-Au1-N6 172.86(13), C22-Au2-N3 172.84(13). The *boat* conformation is shown.

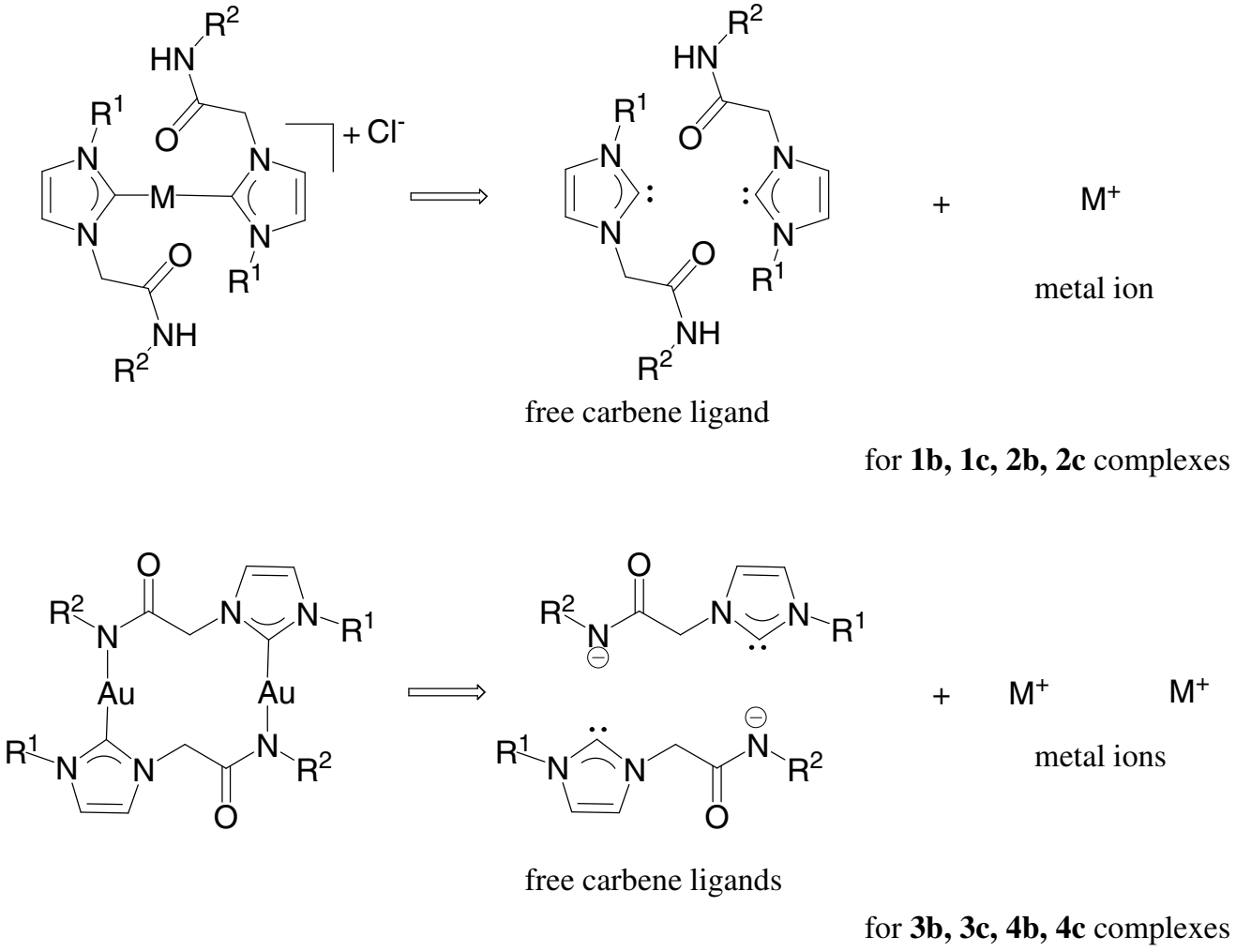


Figure S5. Fragmentation scheme used in the DFT studies of the **1b**, **1c**, **2b**, **2c**, **3b**, **3c**, **4b** and **4c** compl,exes.

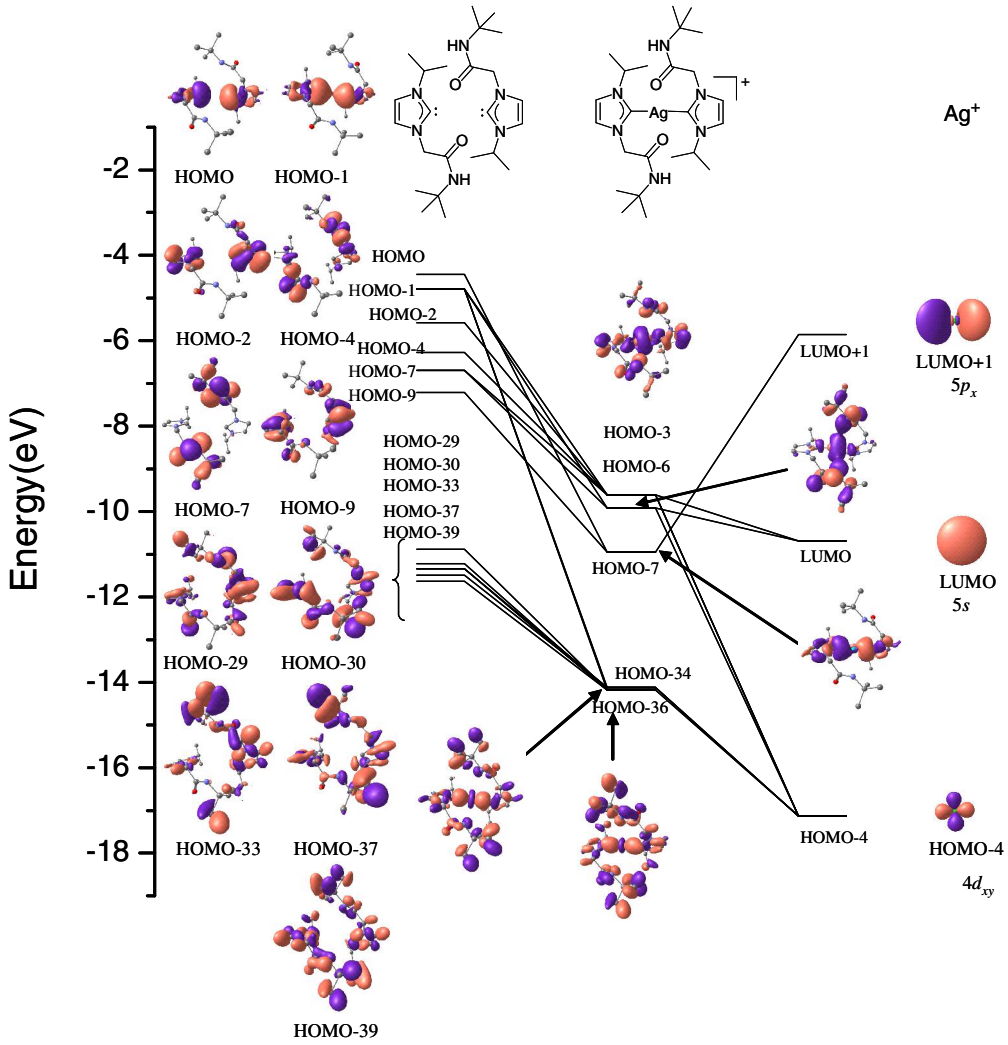


Figure S6. Simplified orbital interaction diagram showing the major contributions of NHC-silver bond in **1b**.

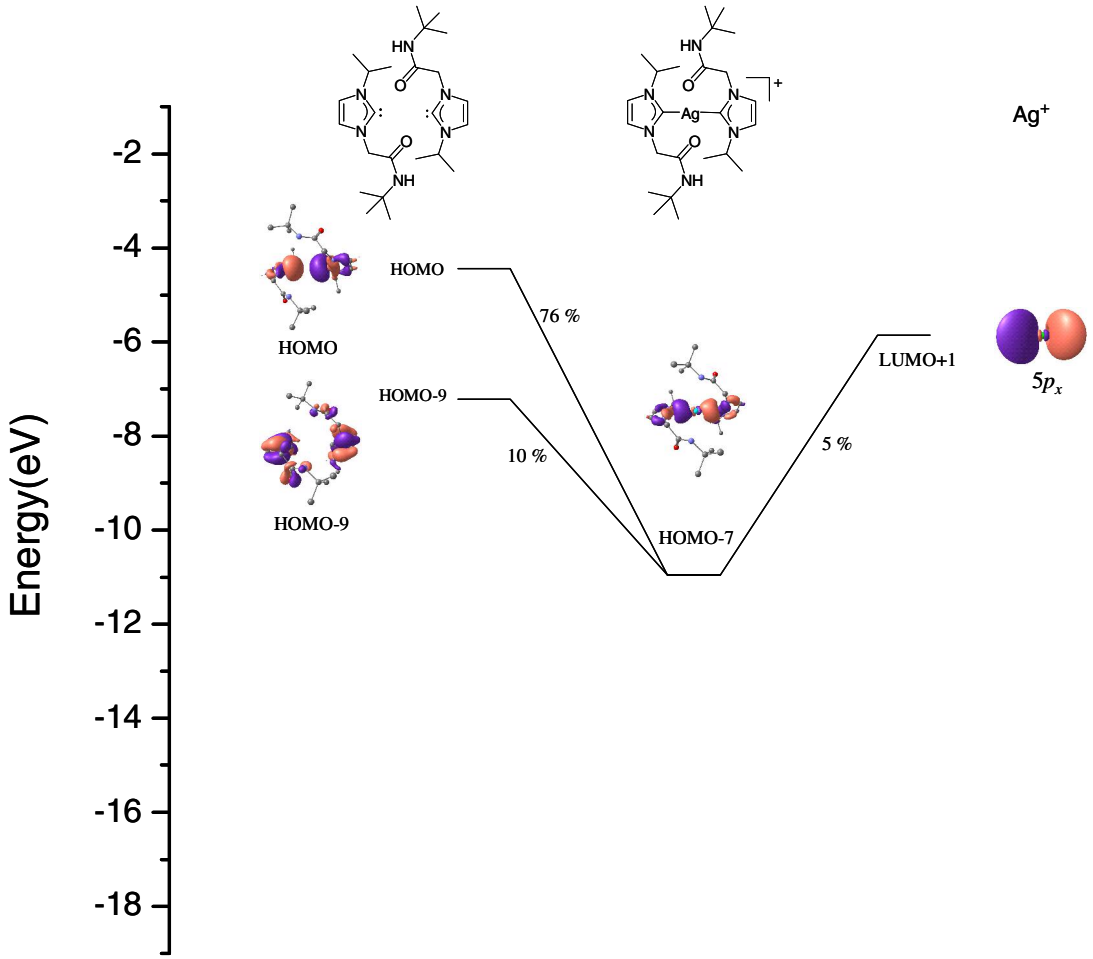


Figure S7. Orbital interaction diagram showing the major contribution of NHC-silver bond in **1b**.

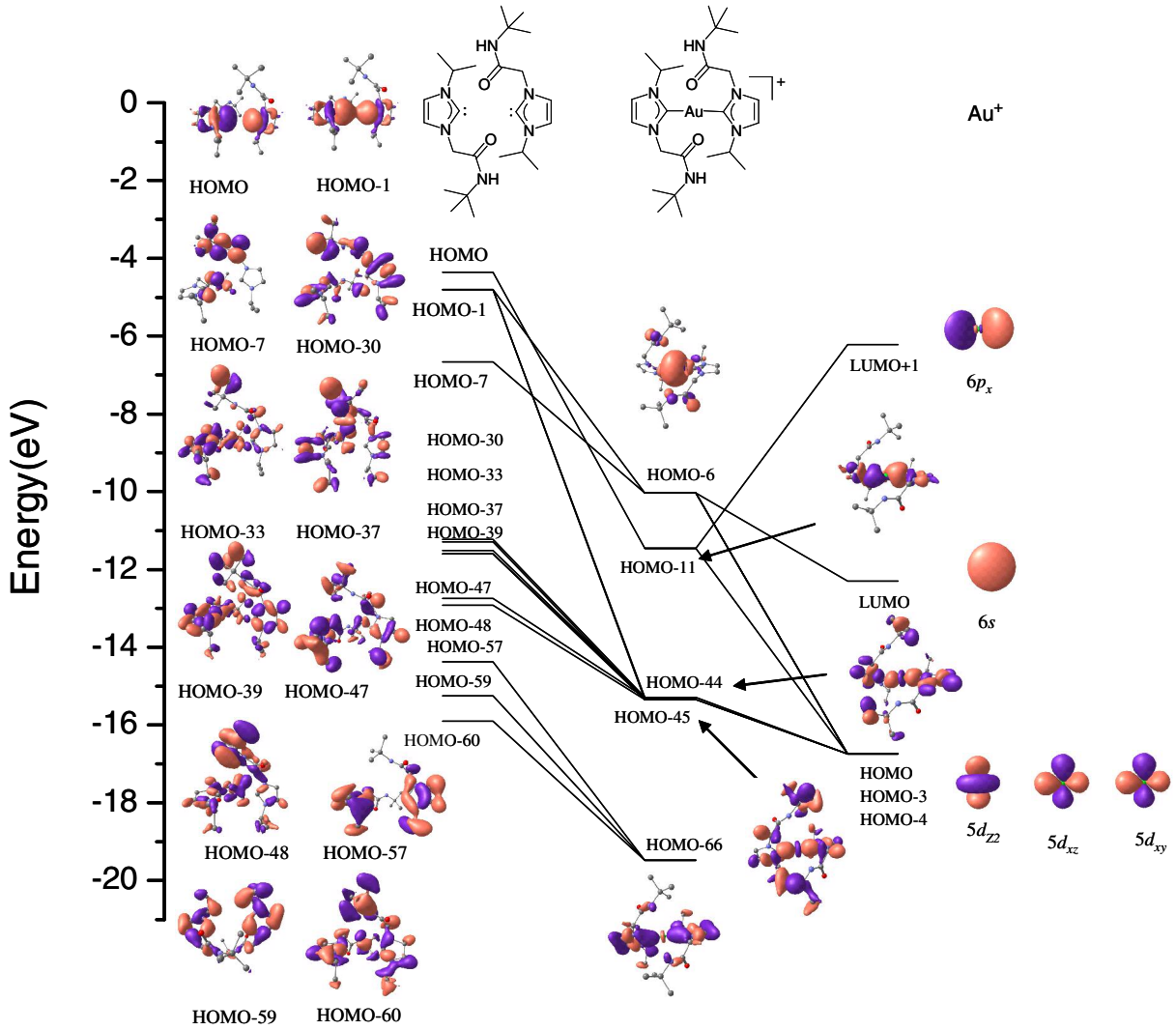


Figure S8. Simplified orbital interaction diagram showing the major contributions of NHC-gold bond in **1c**.

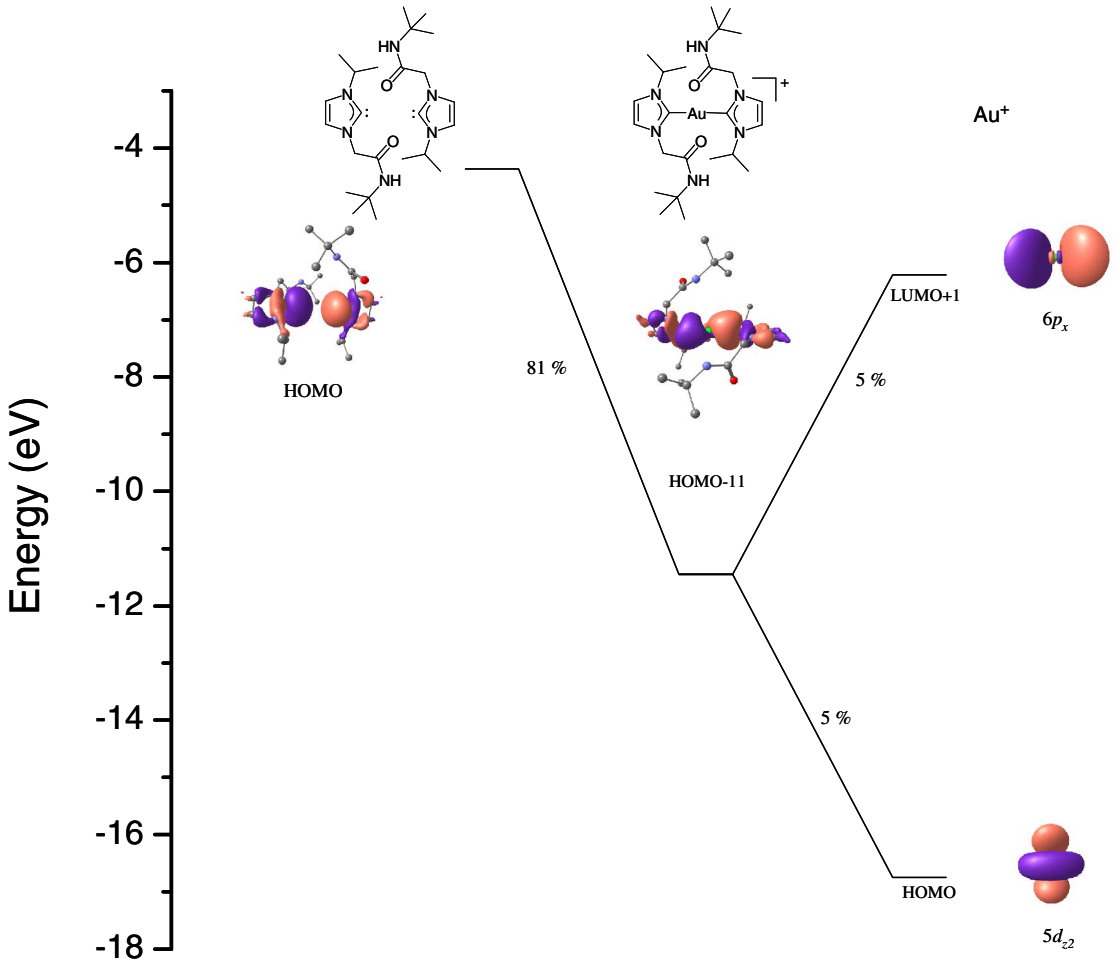


Figure S9. Orbital interaction diagram showing the major contribution of NHC-gold bond in **1c**.

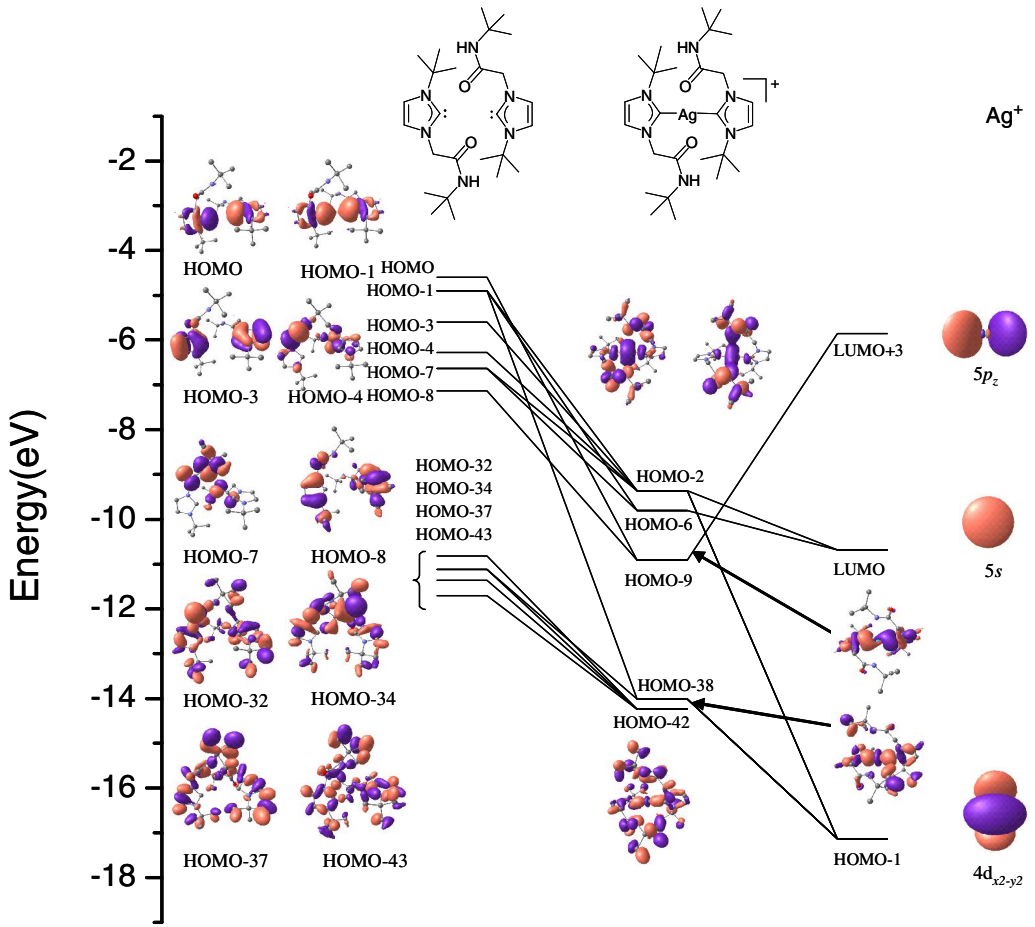


Figure S10. Simplified orbital interaction diagram showing the major contributions of NHC-silver bond in **2b**.

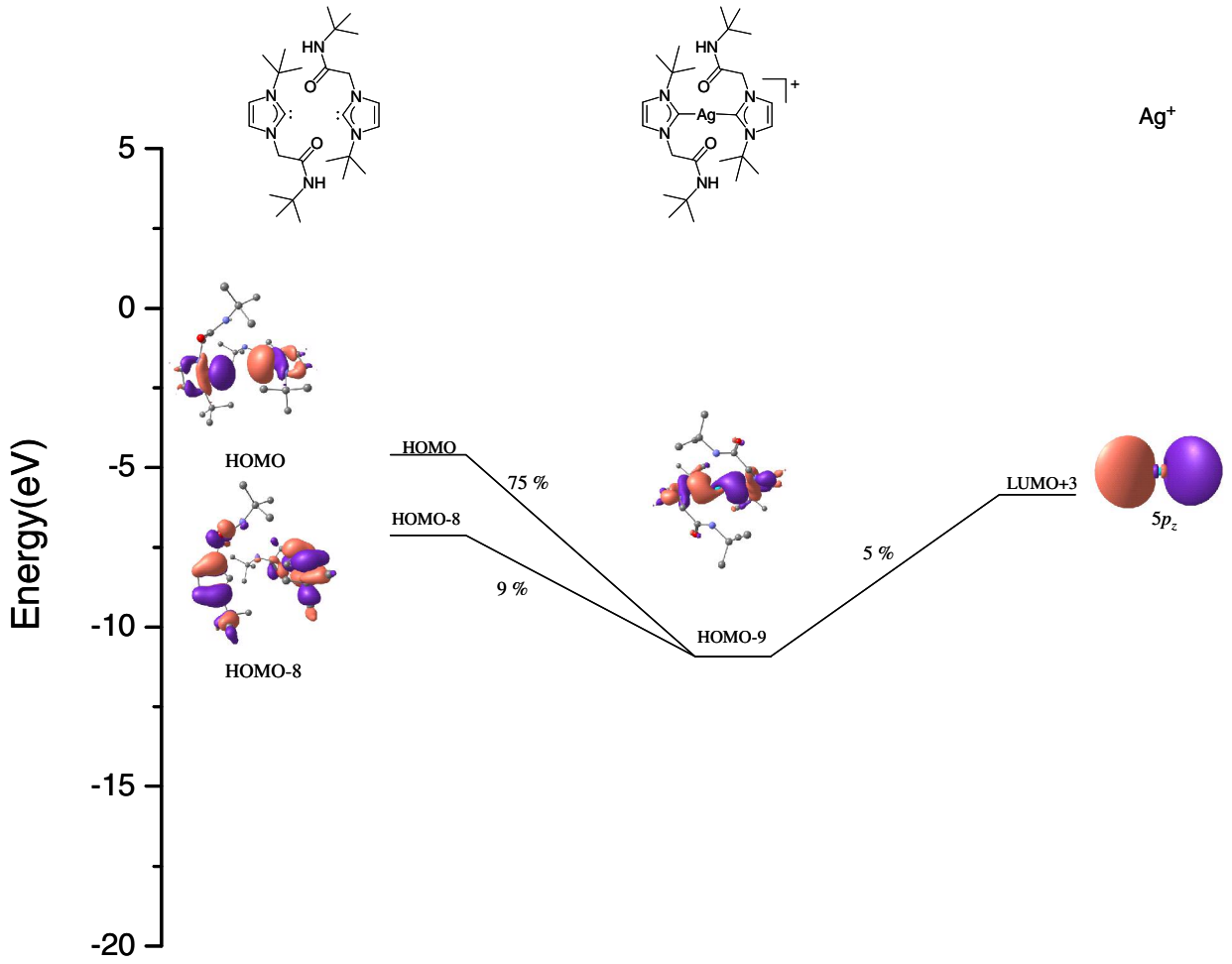


Figure S11. Orbital interaction diagram showing the major contribution of NHC-silver bond in **2b**.

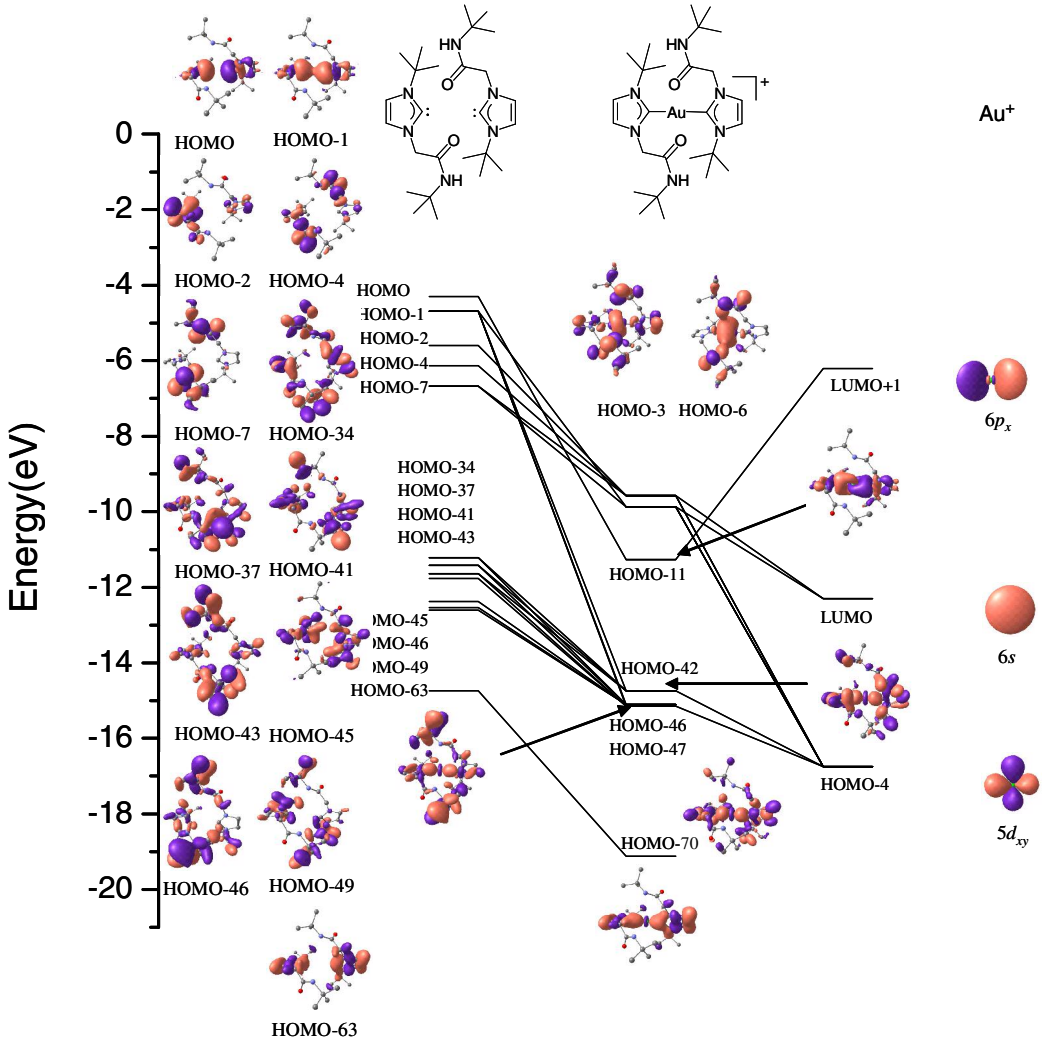


Figure S12. Simplified orbital interaction diagram showing the major contributions of NHC-gold bond in **2c**.

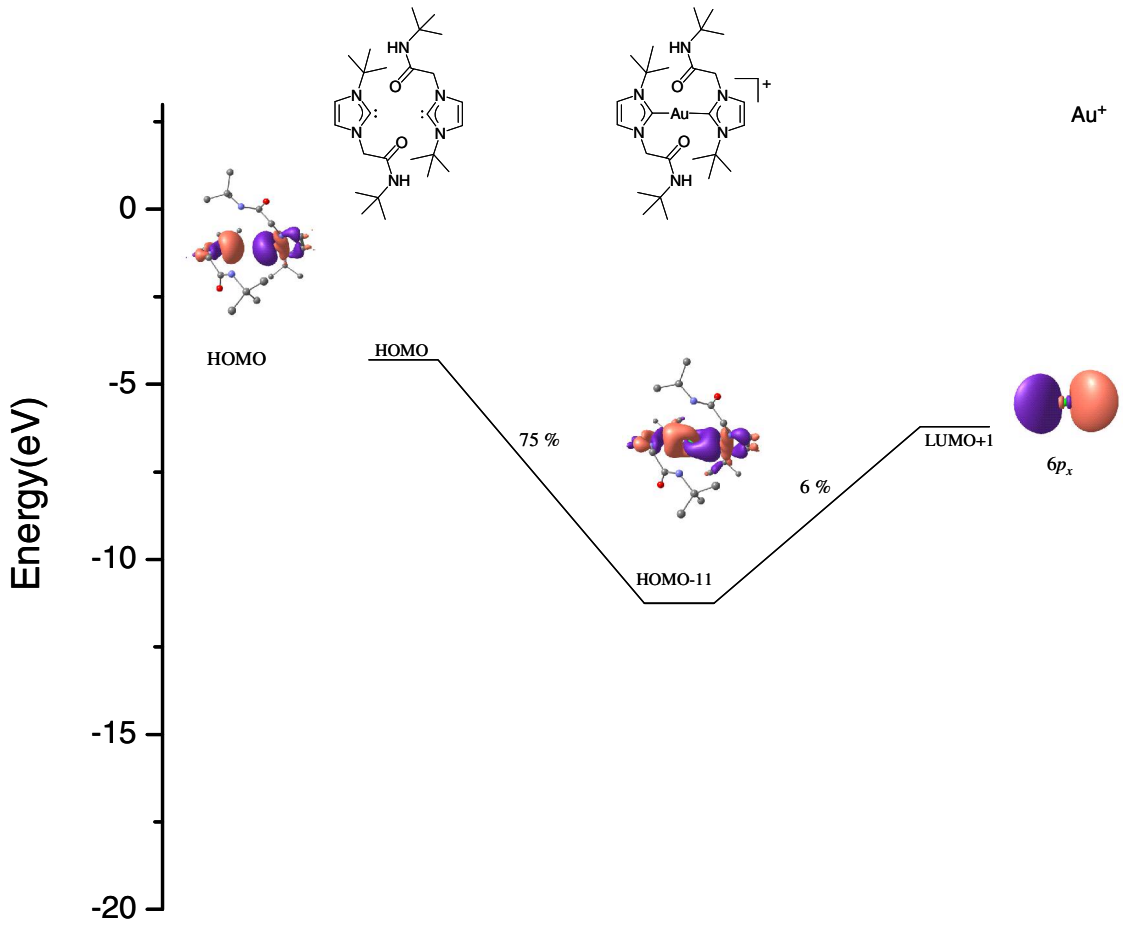


Figure S13. Orbital interaction diagram showing the major contribution of NHC-gold bond in **2c**.

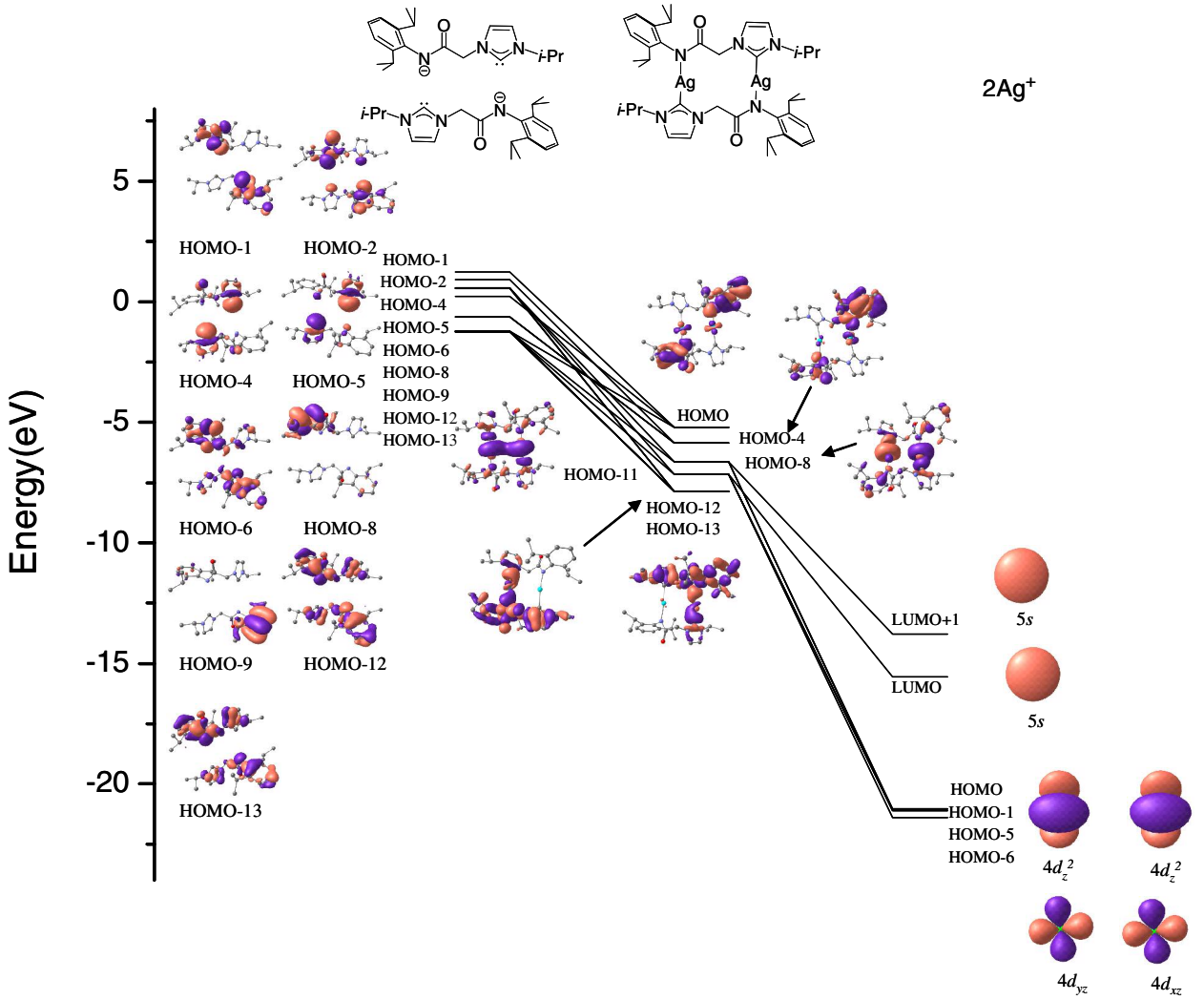


Figure S14. Simplified orbital interaction diagram showing the major contributions of NHC-silver bond in **3b**.

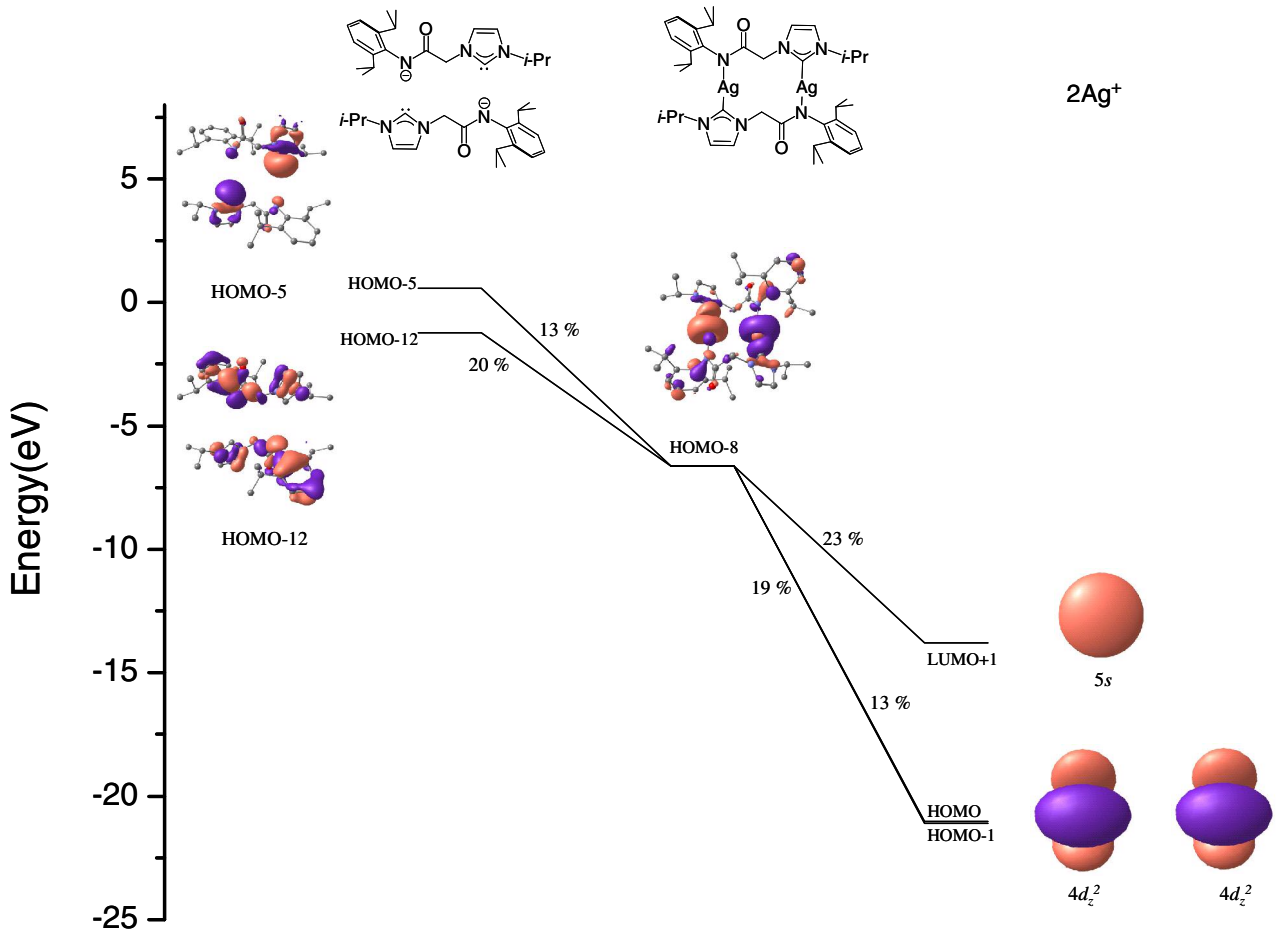


Figure S15. Orbital interaction diagram showing the major contribution of NHC-silver bond in **3b**.

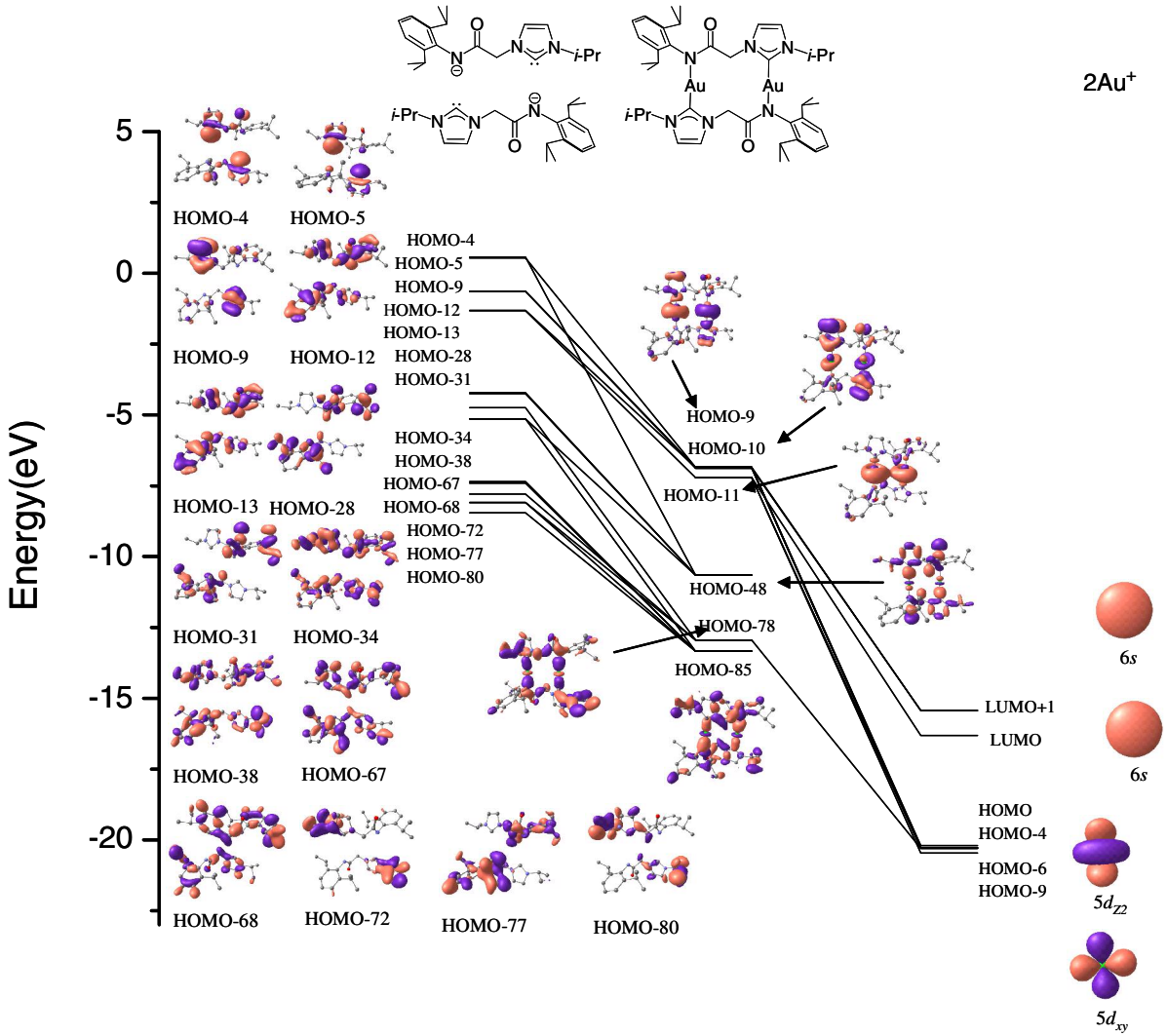


Figure S16. Simplified orbital interaction diagram showing the major contributions of NHC-gold bond in **3c**.

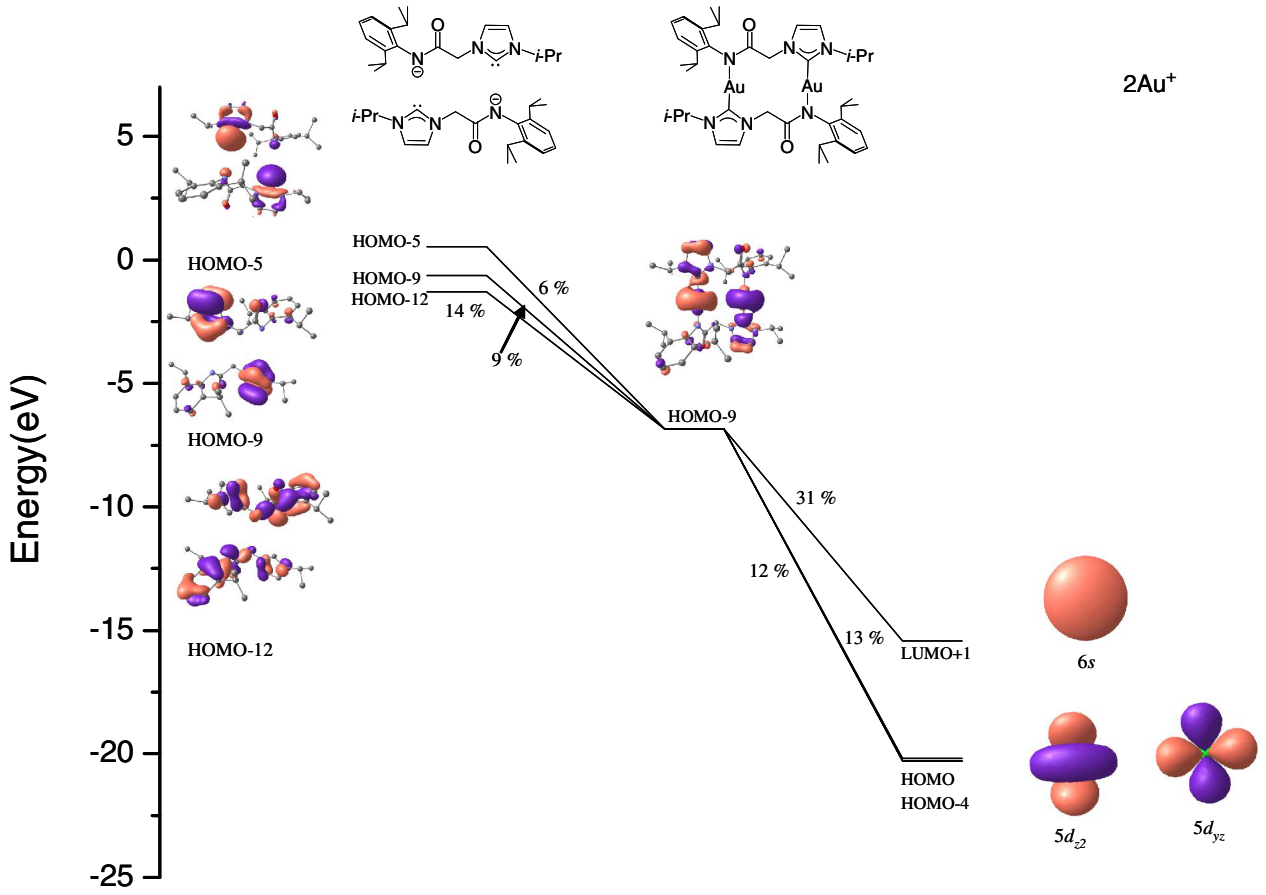


Figure S17. Orbital interaction diagram showing the major contribution of NHC-gold bond in **3c**.

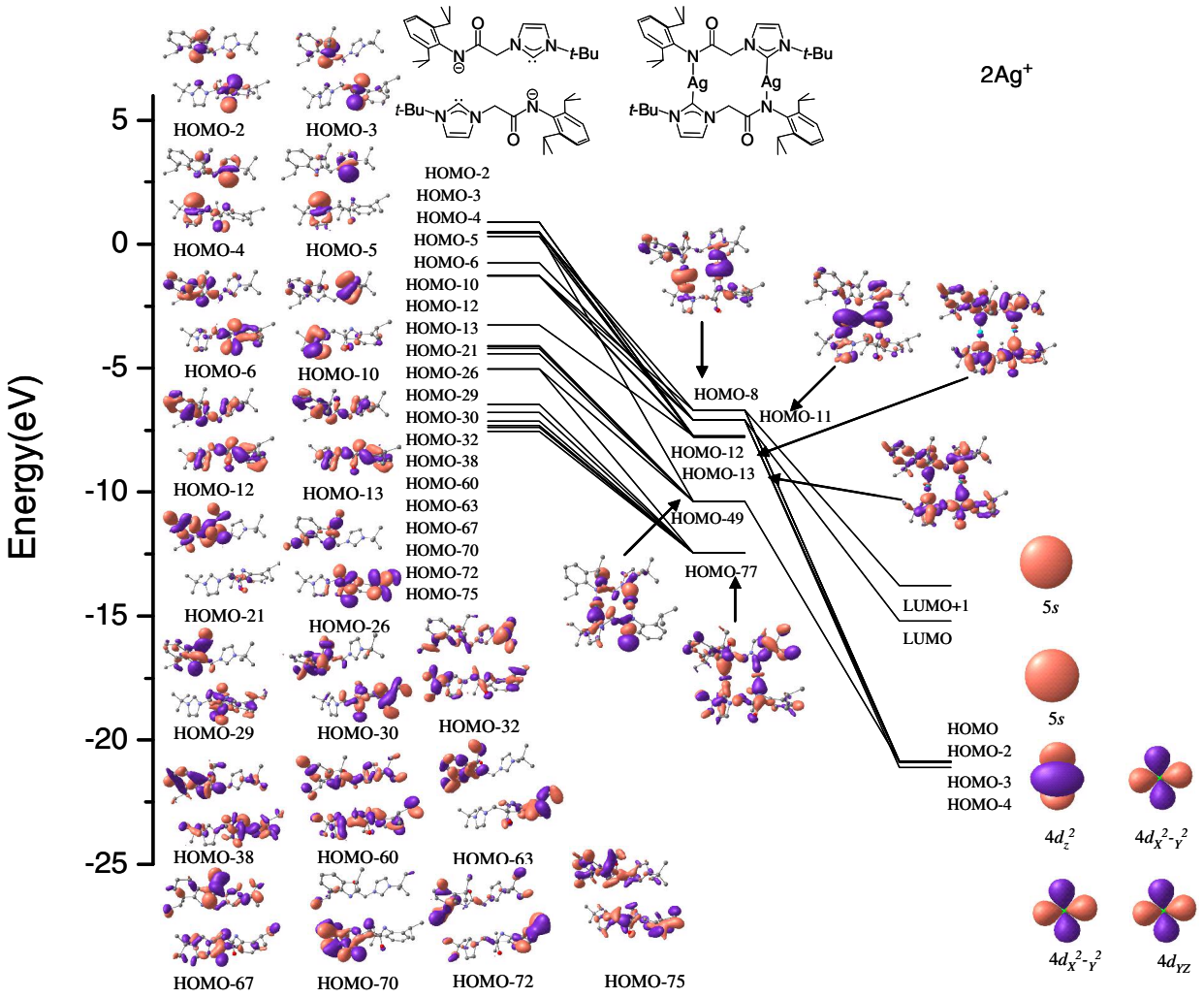


Figure S18. Simplified orbital interaction diagram showing the major contributions of NHC-silver bond in **4b**.

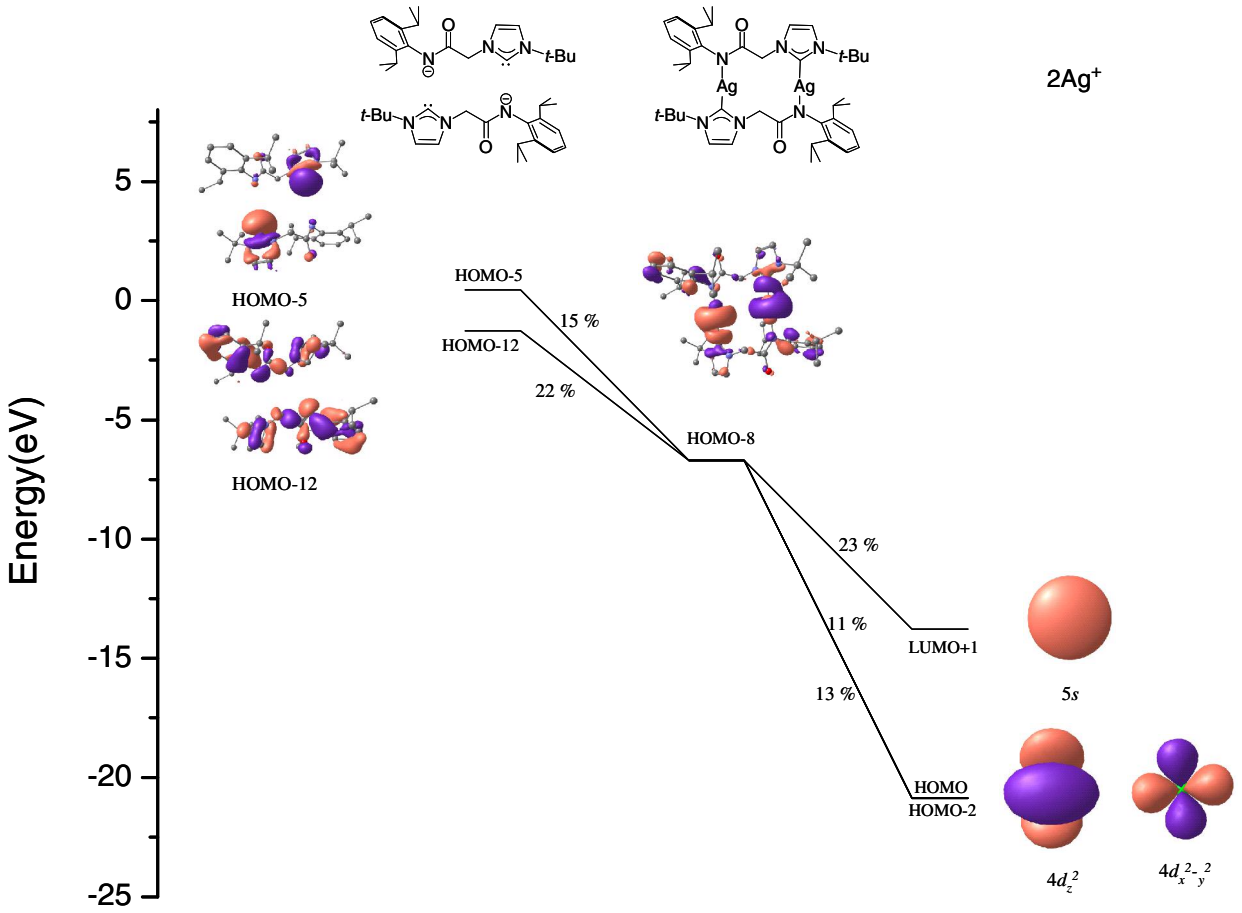


Figure S19. Orbital interaction diagram showing the major contribution of NHC-silver bond in **4b**.

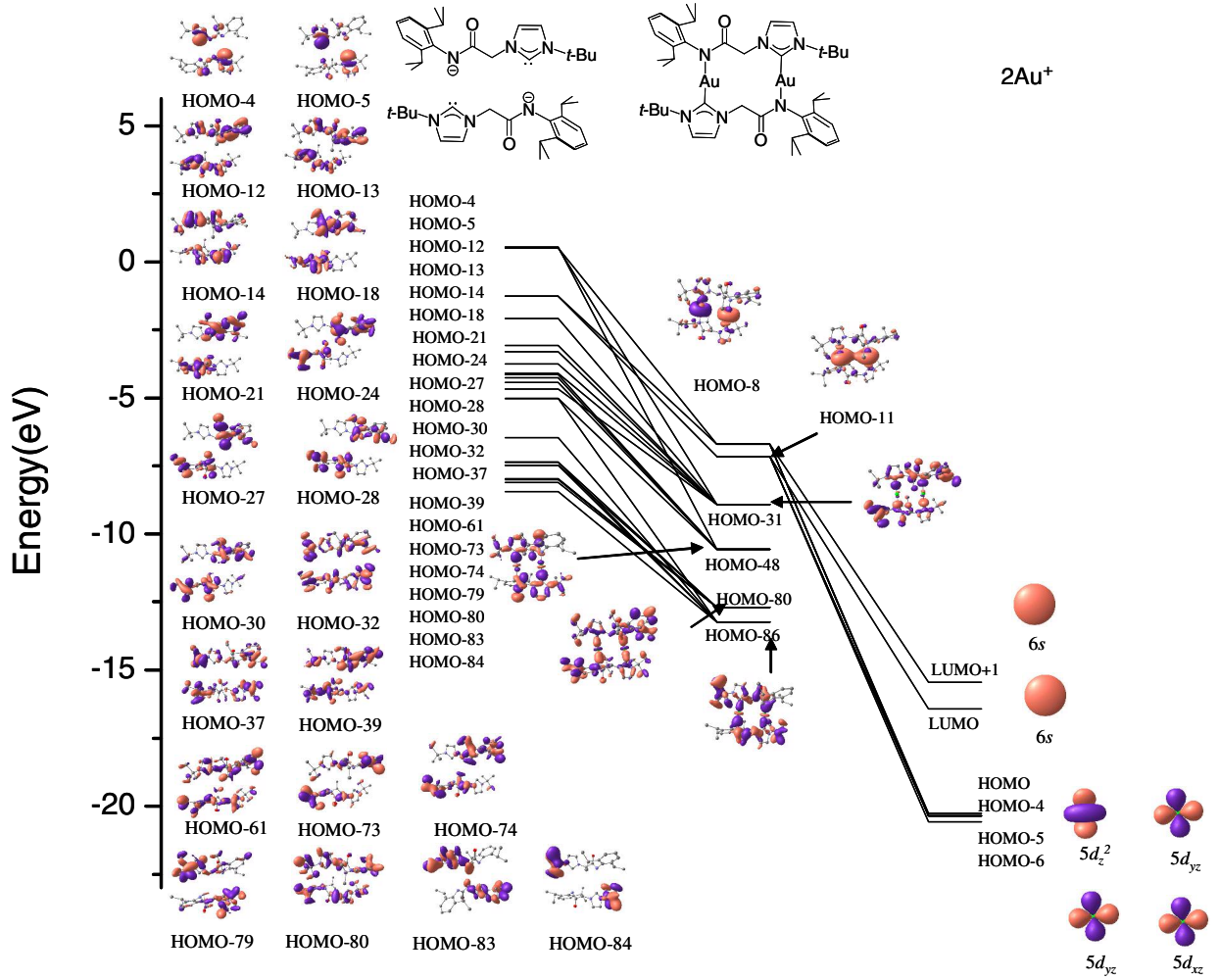


Figure S20. Simplified orbital interaction diagram showing the major contributions of NHC-gold bond in **4c**.

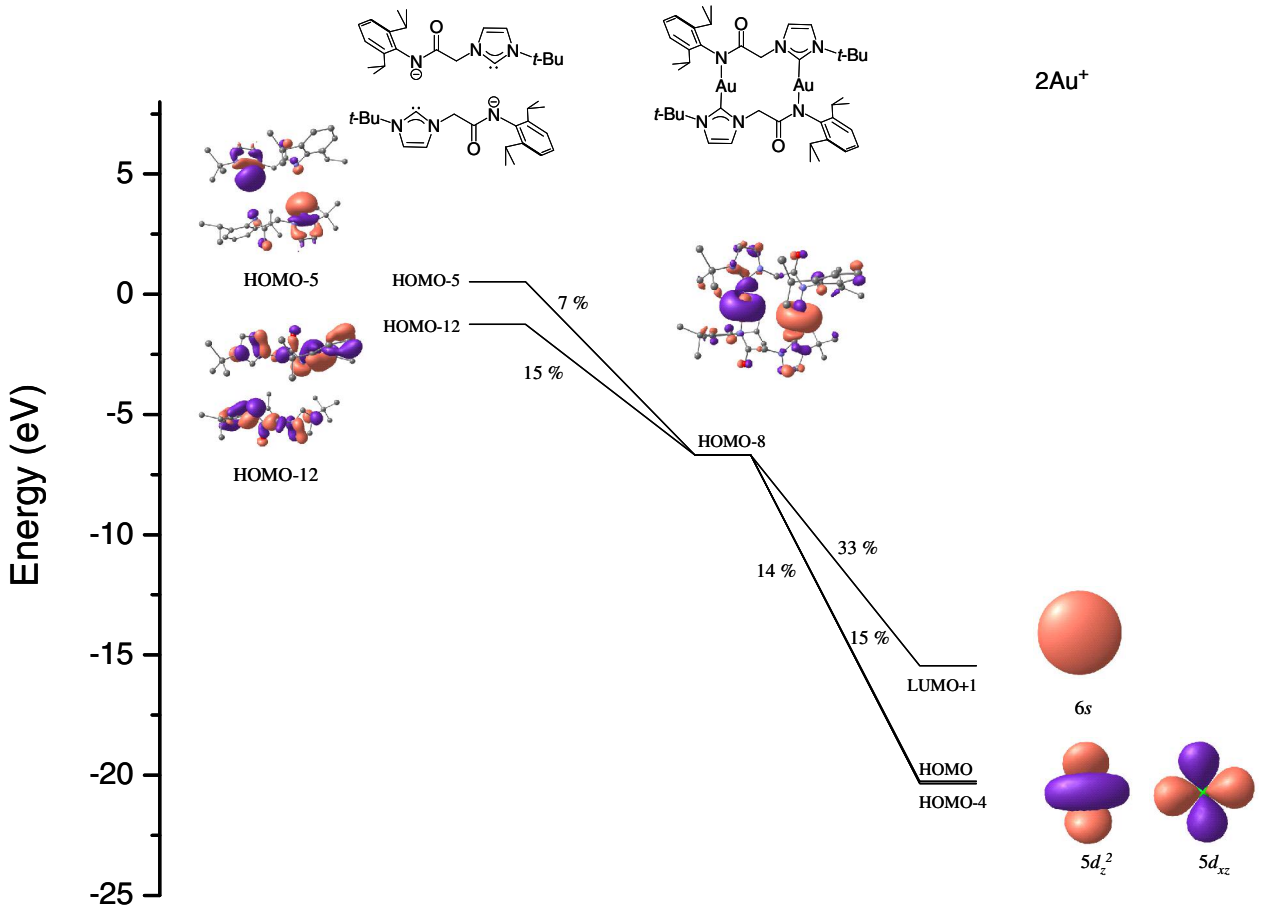


Figure S21. Orbital interaction diagram showing the major contribution of NHC-gold bond in **4c**.

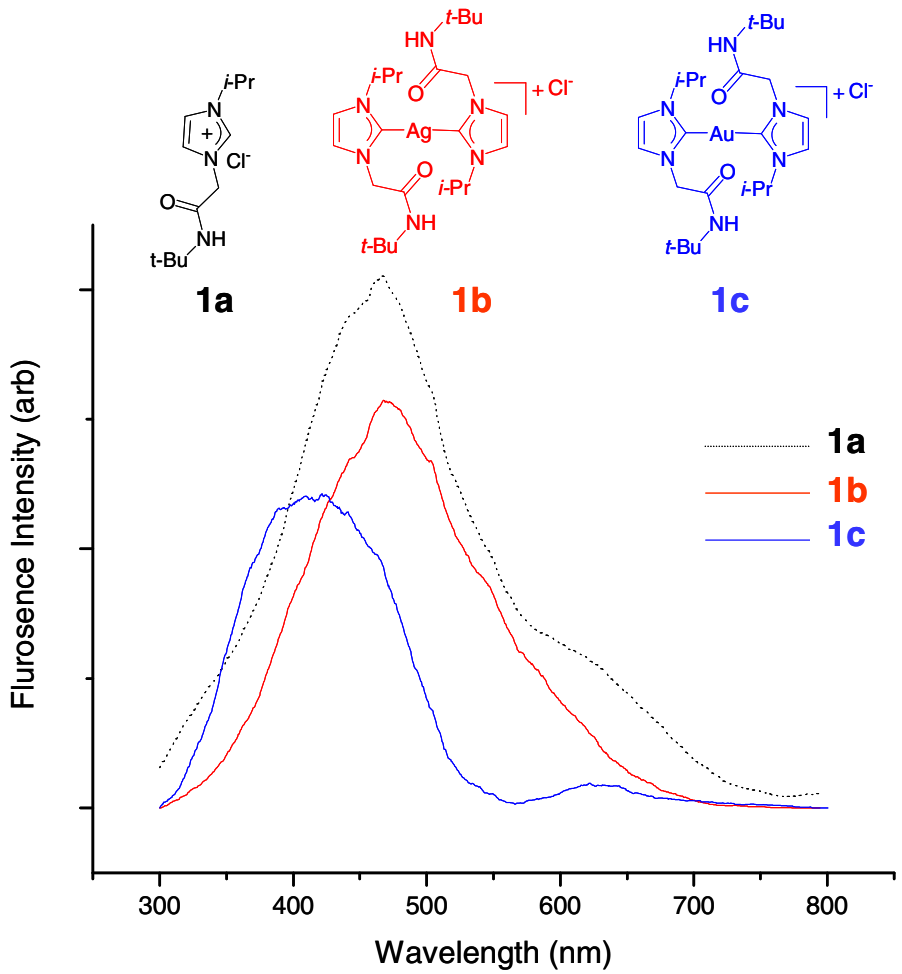


Figure S22. An overlay plot of the emission spectra of the ligand precursor **1a**, the silver complex **1b**, and the gold complex **1c** measured in solid state at room temperature (excitation at 264 nm) is shown.

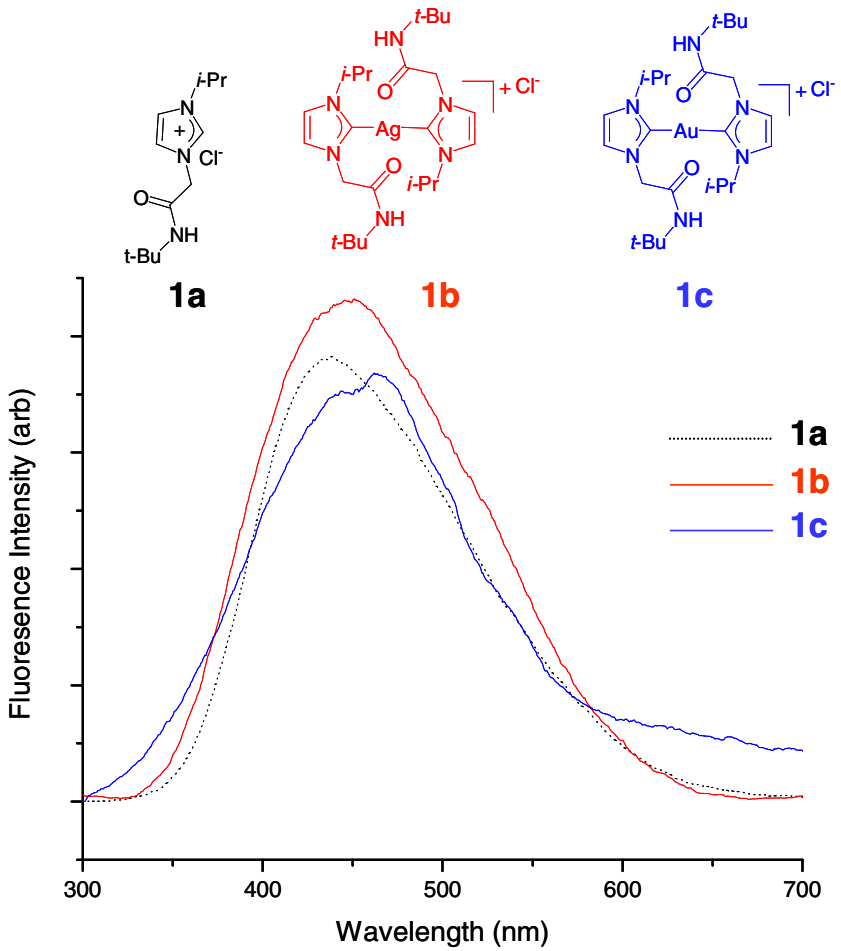


Figure S23. An overlay plot of the emission spectra of the ligand precursor **1a**, the silver complex **1b**, and the gold complex **1c** measured in chloroform ($CHCl_3$) at room temperature (excitation at 264 nm) is shown.

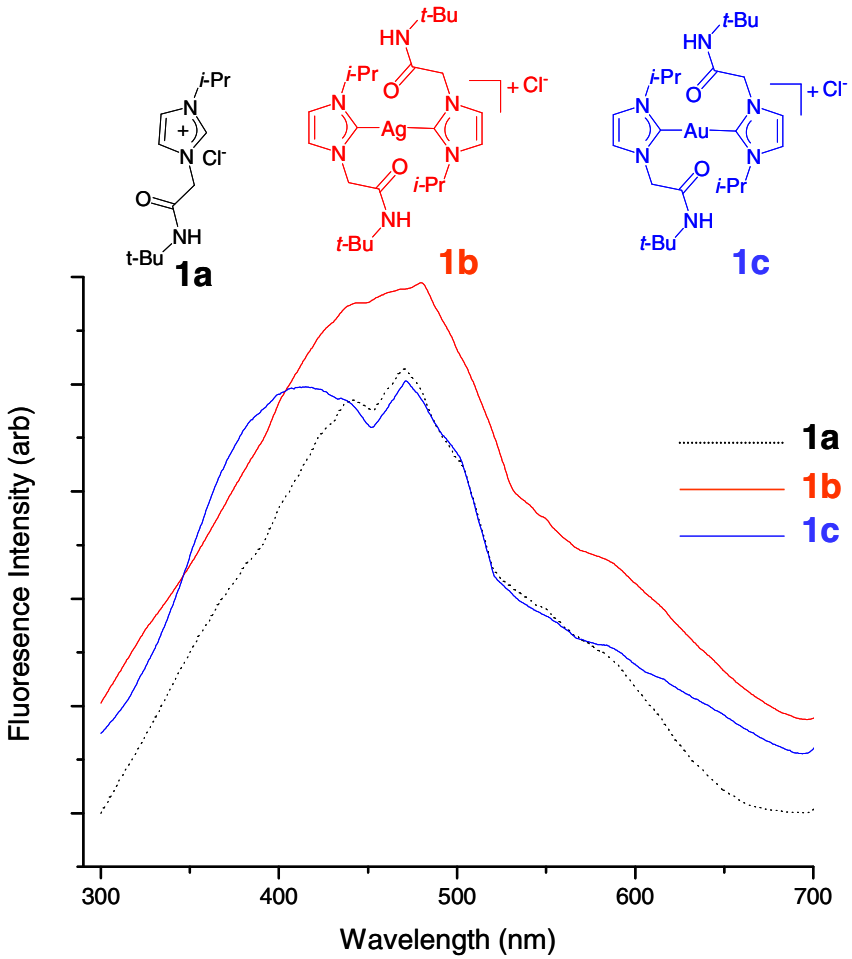


Figure S24. An overlay plot of the emission spectra of the ligand precursor **1a**, the silver complex **1b**, and the gold complex **1c** measured in a glassy solution of EtOH : MeOH (4 : 1, v/v) mixture at low temperature (77 K) (excitation at 244 nm) is shown.

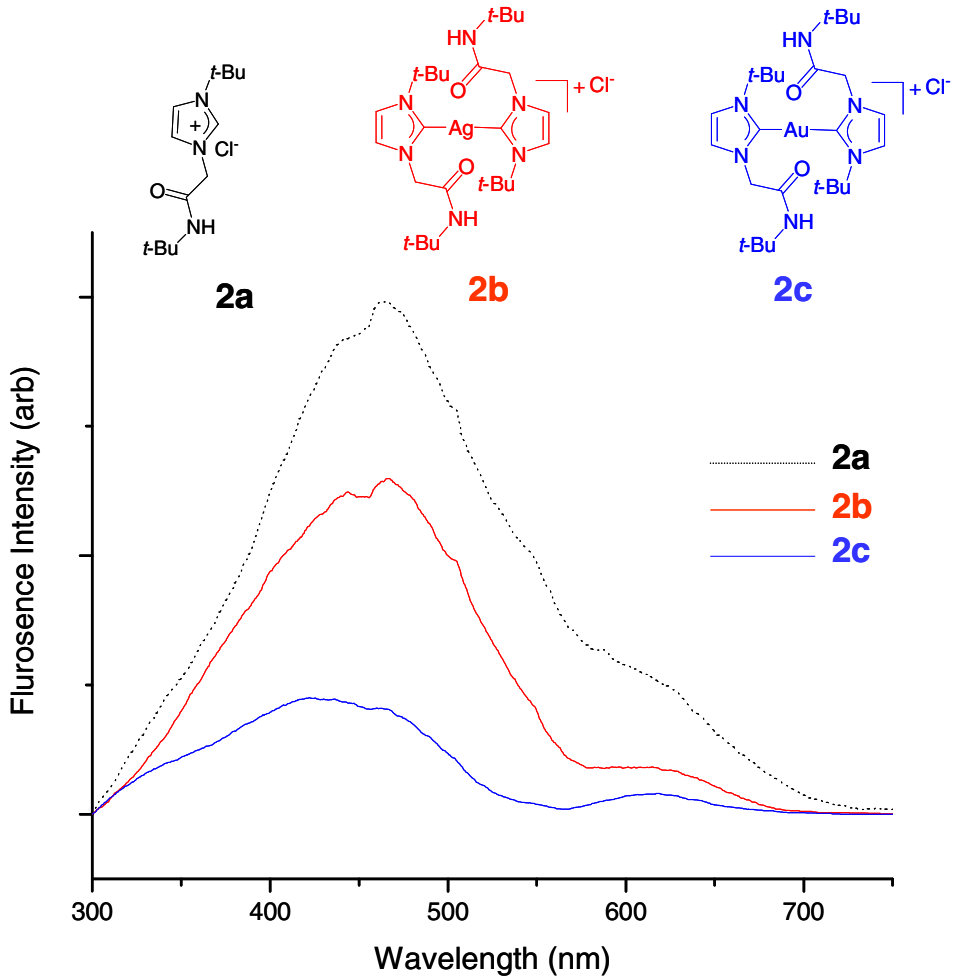


Figure S25. An overlay plot of the emission spectra of the ligand precursor **2a**, the silver complex **2b**, and the gold complex **2c** measured in solid state at room temperature (excitation at 264 nm) is shown.

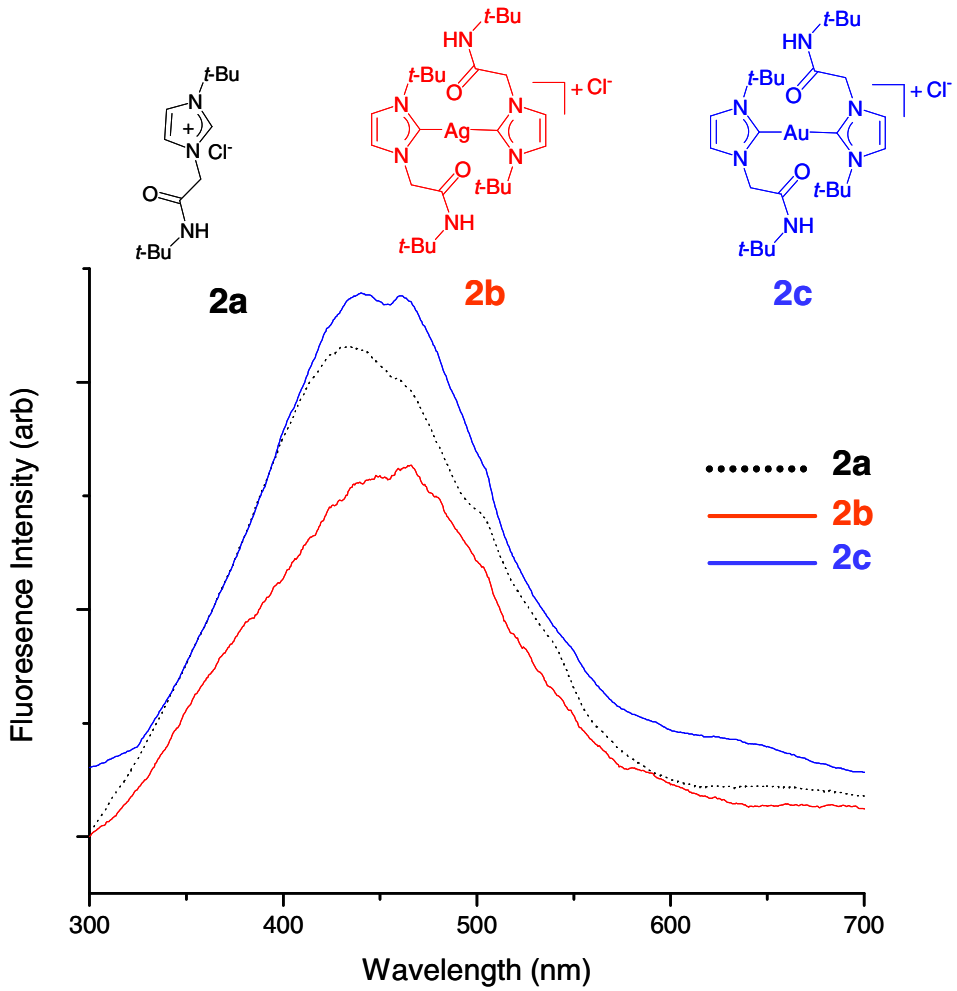


Figure S26. An overlay plot of the emission spectra of the ligand precursor **2a**, the silver complex **2b**, and the gold complex **2c** measured in chloroform ($CHCl_3$) at room temperature (excitation at 264 nm) is shown.

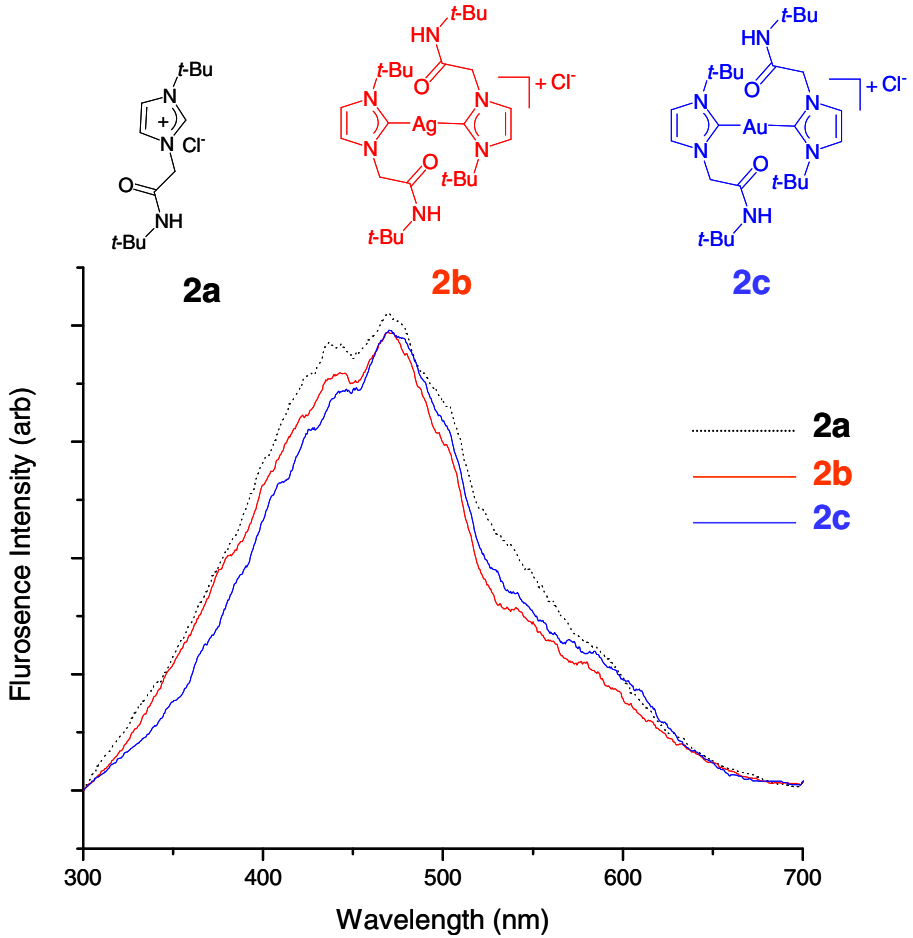


Figure S27. An overlay plot of the emission spectra of the ligand precursor **2a**, the silver complex **2b**, and the gold complex **2c** measured in a glassy solution of EtOH : MeOH (4 : 1, v/v) mixture at low temperature (77 K) (excitation at 244 nm) is shown.

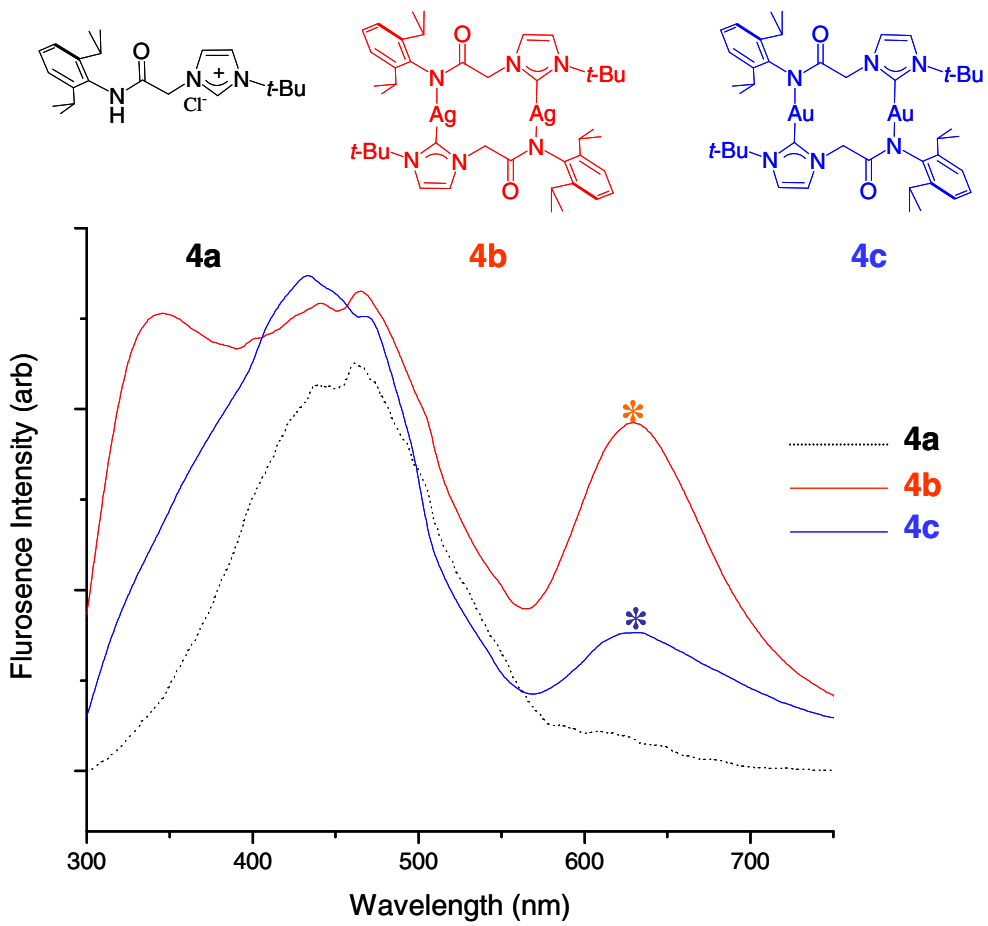


Figure S28. An overlay plot of the emission spectra of the ligand precursor **4a**, the silver complex **4b**, and the gold complex **4c** measured in solid state at room temperature (excitation at 264 nm) is shown. The peak due to tentative M•••M (M = Ag and Au) interaction is marked by * in the plot.

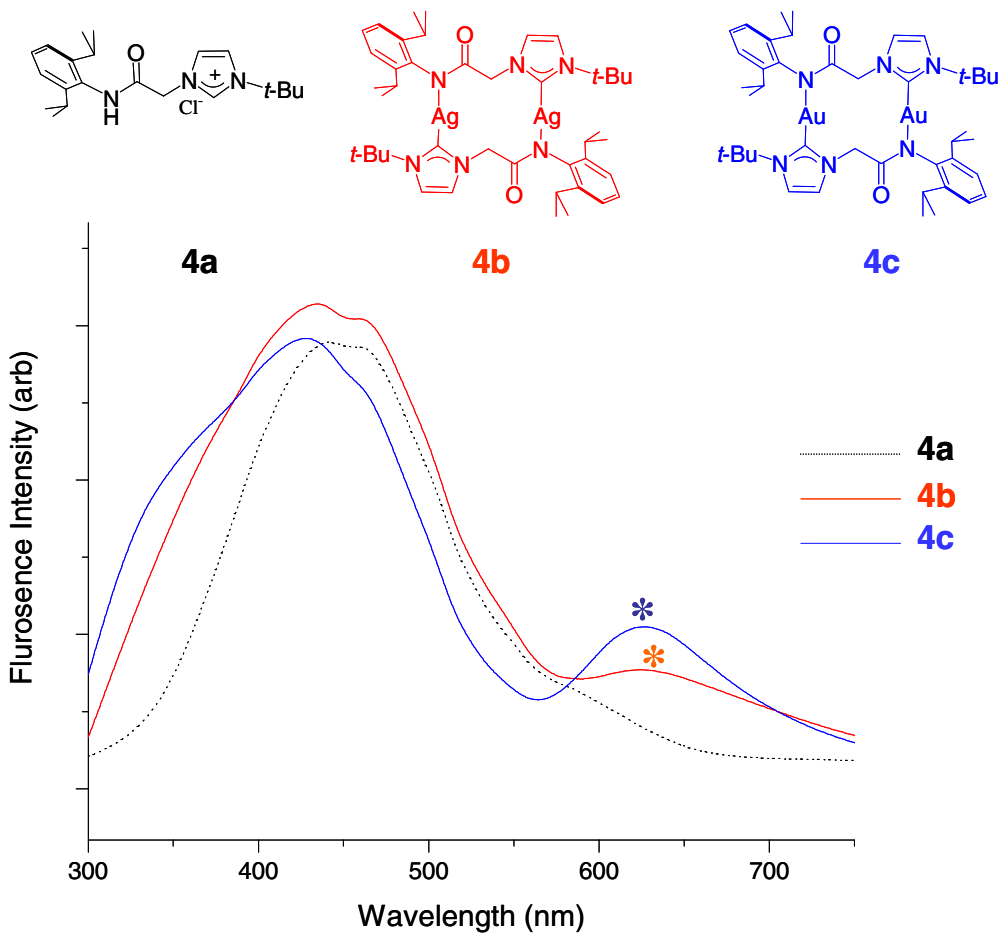


Figure S29. An overlay plot of the emission spectra of the ligand precursor **4a**, the silver complex **4b**, and the gold complex **4c** measured in chloroform ($CHCl_3$) at room temperature (excitation at 264 nm) is shown. The peak due to tentative M•••M (M = Ag and Au) interaction is marked by * in the plot.

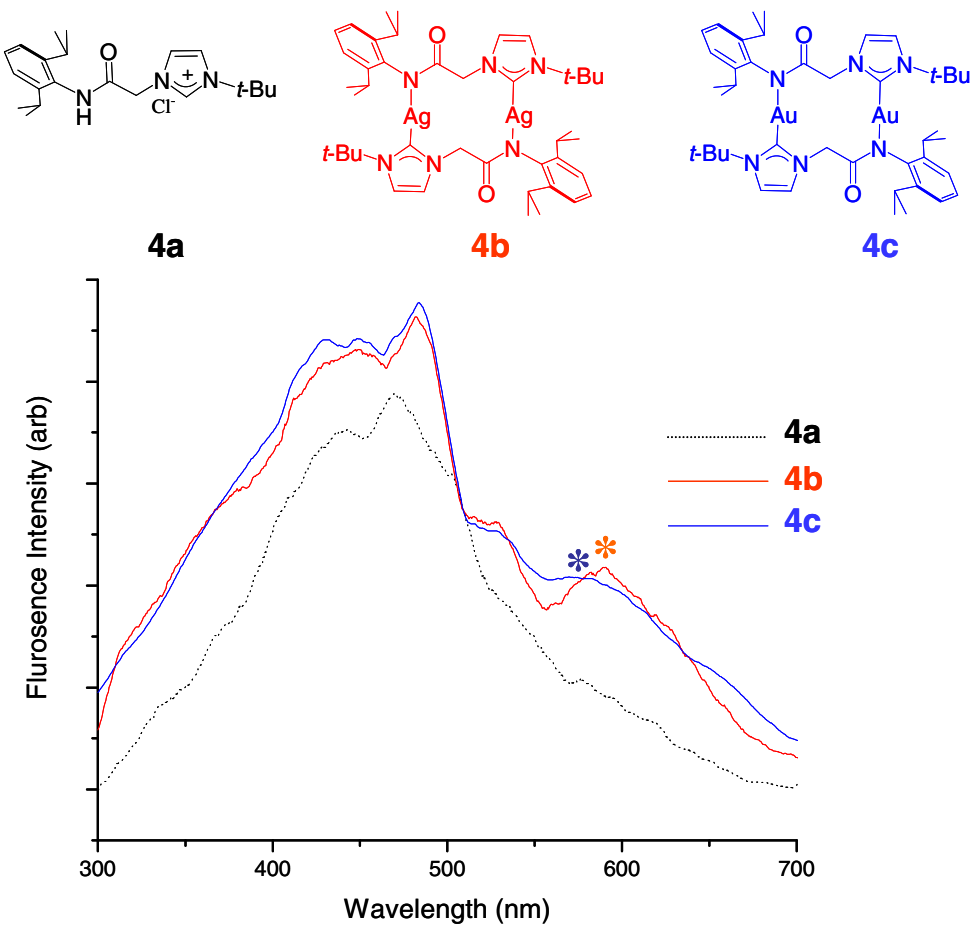


Figure S30. An overlay plot of the emission spectra of the ligand precursor **4a**, the silver complex **4b**, and the gold complex **4c** measured in a glassy solution of EtOH : MeOH (4 : 1, v/v) mixture at low temperature (77 K) (excitation at 244 nm) is shown. The peak due to tentative M•••M (M = Ag and Au) interaction is marked by * in the plot.

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[1]. GAUSSIAN 03: Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.