Supporting Information

An ab initio study on coinage atom-inserted cyanide/isocyanide: XMCN/XMNC (M = coinage atoms; X = halogen)

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Table S1. The selected vibrational frequencies of XMCN and XMNC (X = halogens, M = Ag and Au) and the concerning precursors calculated at the CCSD(T) level [a].

	XMCN					XMNC			
	ν_{C-N}	$\Delta\nu_{C-N}$ [b]	ν_{M-C}	ν_{X-M}		ν_{C-N}	$\Delta\nu_{C-N}$ [b]	ν_{M-N}	ν_{X-M}
FAgCN	2338.6	-29.2	428.7	582.7	FAgNC	2115.2	-76.7	441.9	577.3
ClAgCN	2188.4	-75.2	412.6	304.7	ClAgNC	2102.6	-34.8	435.8	265.5
BrAgCN	2193.6	-47.0	403.3	164.8	BrAgNC	2113.1	-6.6	425.1	165.4
IAgCN	2196.4	-24.0	395.8	136.5	IAgNC	2124.7	12.1	415.4	143.9
FAuCN	2310.1	-57.7	461.5	576.8	FAuNC	2132.8	-59.1	484.4	595.5
ClAuCN	2430.1	166.6	463.9	337.5	ClAuNC	2115.3	-22.1	475.4	559.2
BrAuCN	2235.7	-4.9	451.2	208.4	BrAuNC	2086.4	-33.2	469.7	239.8
IAuCN	2218.3	-2.1	444.1	156.5	IAuNC	2116.1	3.4	457.4	182.3
FCN	2367.8				FNC	2191.9			
ClCN	2263.6				ClNC	2137.4			
BrCN	2240.6				BrNC	2119.7			
ICN	2220.4				INC	2112.6			

[a] Frequencies are in cm^{-1} and intensities (in parentheses) are in $km \cdot mol^{-1}$.

[b] $\Delta\nu_{C-N}$ is the difference of the ν_{C-N} between XMCN (or XMNC) and XCN (or XNC).

Table S2. The AIM results of XAgCN and XAgNC (X = halogens) calculated using the CCSD(T) method with all-electron relativistic basis sets [a].

molecule	bond	$\rho(r)$	$\nabla^2\rho(r)$	H(r)	$\lvert V(r)\rvert/G(r)$	molecule	bond	$\rho(r)$	$\nabla^2\rho(r)$	H(r)	$\lvert V(r)\rvert/G(r)$
FAgCN	F–Ag	0.128	0.693	-0.045	1.207	FAgNC	F–Ag	0.132	0.698	-0.049	1.220
	Ag–C	0.139	0.279	-0.075	1.517		Ag–N	0.129	0.533	-0.052	1.280
	C–N	0.485	0.148	-0.948	1.963		C–N	0.460	-0.193	-0.882	2.058
ClAgCN	Cl–Ag	0.097	0.256	-0.031	1.330	ClAgNC	Cl–Ag	0.093	0.365	-0.028	1.233
	Ag–C	0.132	0.230	-0.066	1.533		Ag–N	0.120	0.525	-0.041	1.236
	C–N	0.480	0.189	-0.935	1.952		C–N	0.466	-0.254	-0.901	2.076
BrAgCN	Br–Ag	0.076	0.159	-0.021	1.348	BrAgNC	Br–Ag	0.081	0.138	-0.026	1.428
	Ag–C	0.126	0.232	-0.061	1.514		Ag–N	0.115	0.453	-0.041	1.264
	C–N	0.483	0.174	-0.940	1.956		C–N	0.460	-0.184	-0.882	2.055
IAgCN	I–Ag	0.055	0.142	-0.011	1.230	IAgNC	I–Ag	0.061	0.151	-0.013	1.259
	Ag–C	0.116	0.308	-0.049	1.389		Ag–N	0.110	0.491	-0.033	1.214
	C–N	0.487	0.056	-0.952	1.985		C–N	0.468	-0.232	-0.906	2.068

[a] The recontracted scalar relativistic def2-TZVPP basis sets were used for all atoms.

Table S3. The AIM results of XAuCN and XAuNC (X = halogens) calculated using the CCSD(T) method with all-electron relativistic basis sets [a].

molecule	bond	$\rho(r)$	$\nabla^2\rho(r)$	H(r)	$\lvert V(r)\rvert/G(r)$	molecule	bond	$\rho(r)$	$\nabla^2\rho(r)$	H(r)	$\lvert V(r)\rvert/G(r)$
FAuCN	F–Au	0.136	0.703	-0.049	1.217	FAuNC	F–Au	0.140	0.720	-0.052	1.226
	Au–C	0.163	0.278	-0.095	1.578		Au–N	0.150	0.580	-0.066	1.311
	C–N	0.485	0.157	-0.948	1.960		C–N	0.454	-0.077	-0.863	2.023
ClAuCN	Cl–Au	0.112	0.239	-0.049	1.451	ClAuNC	Cl–Au	0.135	0.288	-0.065	1.475
	Au–C	0.156	0.265	-0.088	1.569		Au–N	0.157	0.550	-0.070	1.337
	C–N	0.485	0.165	-0.946	1.958		C–N	0.449	-0.186	-0.855	2.058
BrAuCN	Br–Au	0.107	0.176	-0.047	1.515	BrAuNC	Br–Au	0.117	0.153	-0.057	1.599
	Au–C	0.161	0.252	-0.092	1.593		Au–N	0.147	0.564	-0.062	1.306
	C–N	0.482	0.151	-0.938	1.961		C–N	0.452	-0.132	-0.859	2.040
IAuCN	I–Au	0.084	0.130	-0.034	1.510	IAuNC	I–Au	0.094	0.130	-0.042	1.562
	Au–C	0.153	0.260	-0.083	1.562		Au–N	0.143	0.526	-0.057	1.303
	C–N	0.485	0.091	-0.949	1.976		C–N	0.459	-0.140	-0.879	2.041

[a] The recontracted scalar relativistic def2-TZVPP basis sets were used for all atoms.

Table S4. Charge decomposition analysis (CDA) results for XAgCN and XAgNC (X = F, Cl, Br and I) obtained using the MP2 level of theory.

	FAgCN		ClAgCN		BrAgCN		IAgCN	
	F->Ag	CN->Ag	Cl->Ag	CN->Ag	Br->Ag	CN->Ag	I->Ag	CN->Ag
d	0.2168	0.3113	0.1227	0.2639	0.3079	0.2391	0.1511	0.2933
b	-0.0030	0.0179	0.0033	0.0083	0.0031	0.0130	0.0076	0.0093
d-b	0.2198	0.2934	0.1194	0.2556	0.3048	0.2261	0.1435	0.2840
r	-0.0650	-0.0644	-0.0866	-0.1473	-0.0321	-0.0381	-0.0573	-0.1139
b+d	0.2138	0.3292	0.1259	0.2722	0.3111	0.2522	0.1587	0.3027

	FAgNC		ClAgNC		BrAgNC		IAgNC	
	F->Ag	NC->Ag	Cl->Ag	NC->Ag	Br->Ag	NC->Ag	I->Ag	NC->Ag
d	0.2221	0.2420	0.3056	0.2049	0.3062	0.2109	0.1623	0.2169
b	-0.0021	0.0054	0.0015	-0.0002	0.0048	0.0000	0.0092	-0.0049
d-b	0.2242	0.2366	0.3041	0.2051	0.3014	0.2109	0.1532	0.2218
r	-0.0655	-0.0819	-0.0184	-0.0610	-0.0168	-0.0610	-0.0673	-0.1190
b+d	0.2200	0.2474	0.3071	0.2047	0.3110	0.2109	0.1715	0.2119

Table S5. Charge decomposition analysis (CDA) results for XAuCN and XAuNC (X = F, Cl, Br and I) obtained using the MP2 level of theory.

	FAuCN		ClAuCN		BrAuCN		IAuCN	
	F->Au	CN->Au	Cl->Au	CN->Au	Br->Au	CN->Au	I->Au	CN->Au
d	0.2116	0.1847	0.2929	0.1629	0.3021	0.1372	0.3474	0.1174
b	-0.0060	0.0133	0.0013	0.0122	0.0047	-0.0058	0.0060	-0.0088
d-b	0.2175	0.1714	0.2916	0.1507	0.2973	0.1431	0.3414	0.1262
r	-0.0693	-0.1297	-0.0651	-0.1208	-0.0442	-0.1294	-0.0404	-0.1515
b+d	0.2056	0.1979	0.2941	0.1752	0.3068	0.1314	0.3534	0.1086
	FAuNC		ClAuNC		BrAuNC		IAuNC	
	F->Au	NC->Au	Cl->Au	NC->Au	Br->Au	NC->Au	I->Au	NC->Au
d	0.2090	0.1790	0.3044	0.1587	0.2996	0.1150	0.3352	0.0762
b	-0.0050	0.0013	0.0034	-0.0026	0.0093	0.0083	0.0101	0.0039
d-b	0.2140	0.1777	0.3010	0.1613	0.2903	0.1067	0.3250	0.0723
r	-0.0720	-0.1223	-0.0665	-0.1104	-0.0608	-0.1349	-0.0526	-0.1804
b+d	0.2040	0.1804	0.3077	0.1561	0.3088	0.1233	0.3453	0.0800

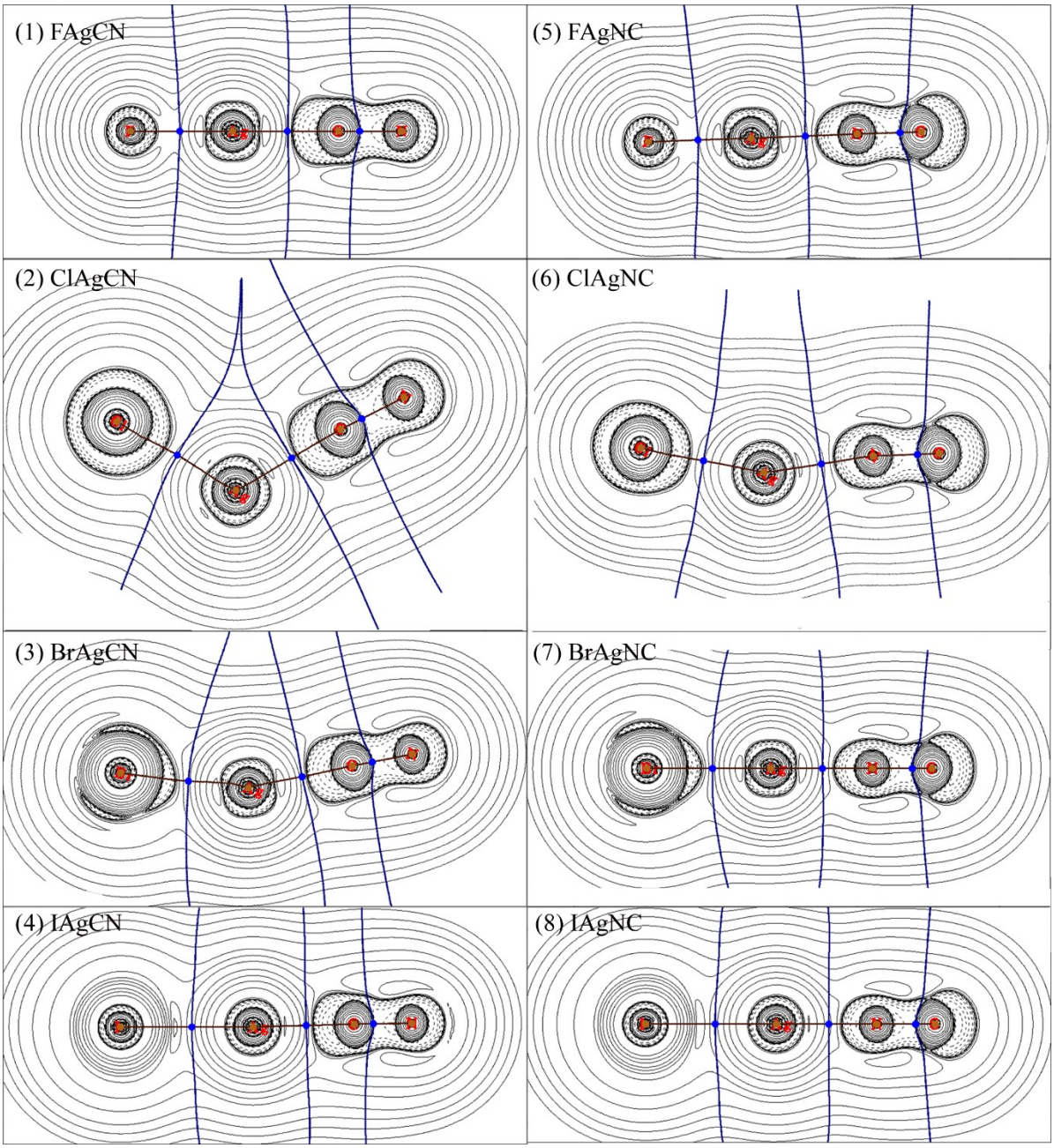

Figure S1. Contour line diagrams of $\nabla^2\rho(r)$ for both XAgCN and XAgNC (X = halogens), obtained by CCSD(T) method with all-electron relativistic basis sets. Dashed lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$) while solid lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The bold brown solid lines connecting the atomic nuclei are the bond paths and the solid blue lines separating the atomic nuclei indicate the zero-flux surfaces in the molecular plane. The crossing points of the bond paths and zero-flux surfaces are the bond critical points (BCP).

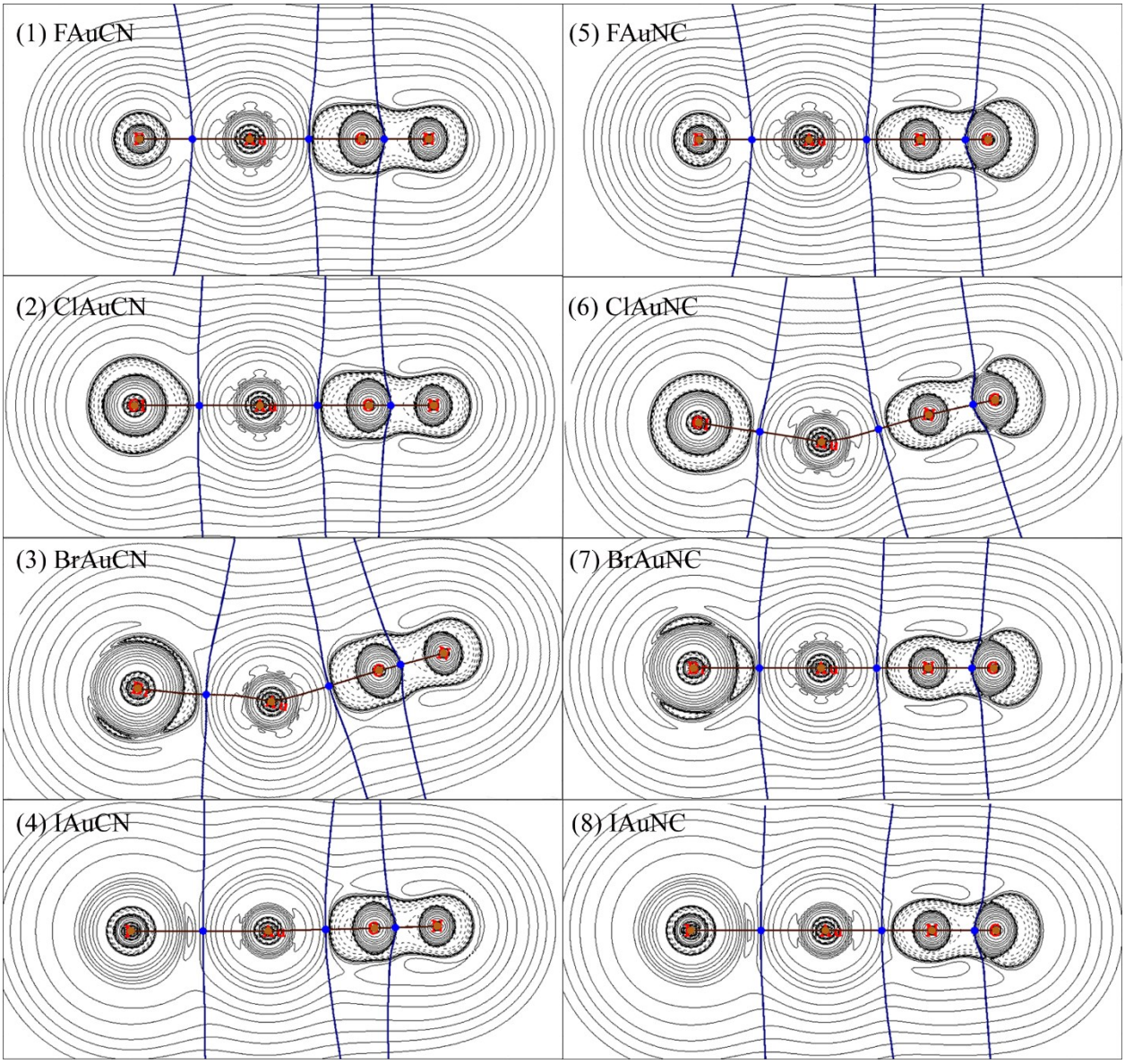

Figure S2. Contour line diagrams of $\nabla^2\rho(r)$ for both XAuCN and XAuNC (X = halogens), obtained by CCSD(T) method with all-electron relativistic basis sets. Dashed lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$) while solid lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The bold brown solid lines connecting the atomic nuclei are the bond paths and the solid blue lines separating the atomic nuclei indicate the zero-flux surfaces in the molecular plane. The crossing points of the bond paths and zero-flux surfaces are the bond critical points (BCP).