

SUPPORTING INFORMATION

Unusually Short Au(III)⋯Au(III) Auophilic Contacts between Anions. Necessity of Counterions

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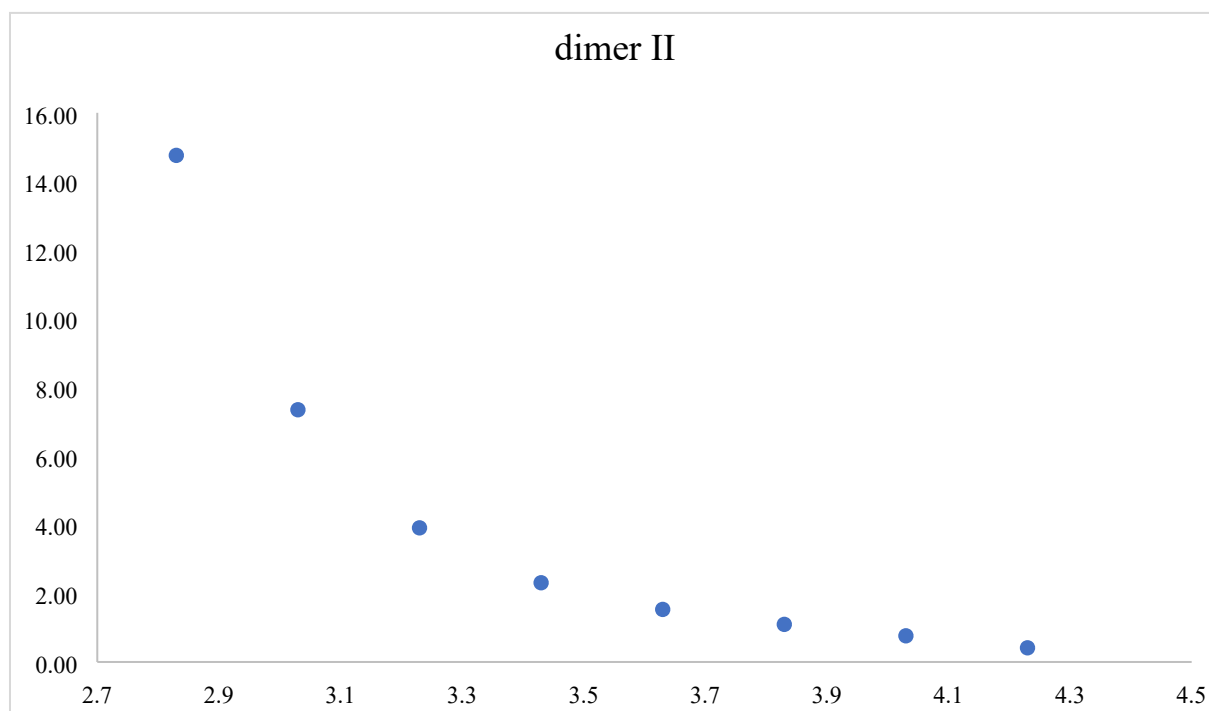


Fig. S1. Trend of the energy versus the Au⋯Au distance calculated at MP2 level for dimer II. Reference (zero) value of energy was set at 4.43 Å.

Table. S1 The energy and the Au...Au distance calculated at M06-2X/de2tzvpp level for the $[\text{Au}(\text{CN})_4]_2^{2-}$ dimer I . Reference (zero) value of energy was set at the distance of 29.5 Å.

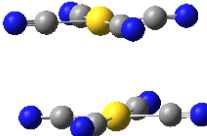
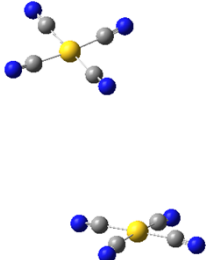
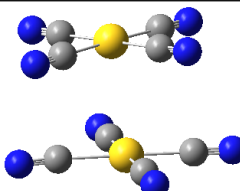
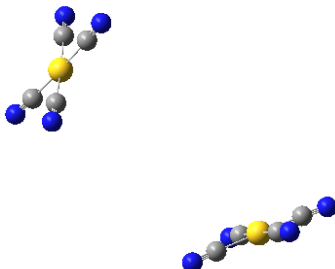
Energy [kcal/mol]	Au...Au distance [Å]	structure
44.33	3.360 (from crystal)	
20.78	9.510	
0.00	29.483	

Table. S2 The energy and the Au...Au distance calculated at M06-2X/de2tzvpp level for the $[\text{Au}(\text{CN})_4]_2^{2-}$ dimer II during full relaxation. Reference (zero) value of energy was set at the distance of 30.1 Å.

Energy [kcal/mol]	Au...Au distance [Å]	structure
44.20	3.435 (from crystal)	
17.57	10.451	
0.00	30.128	

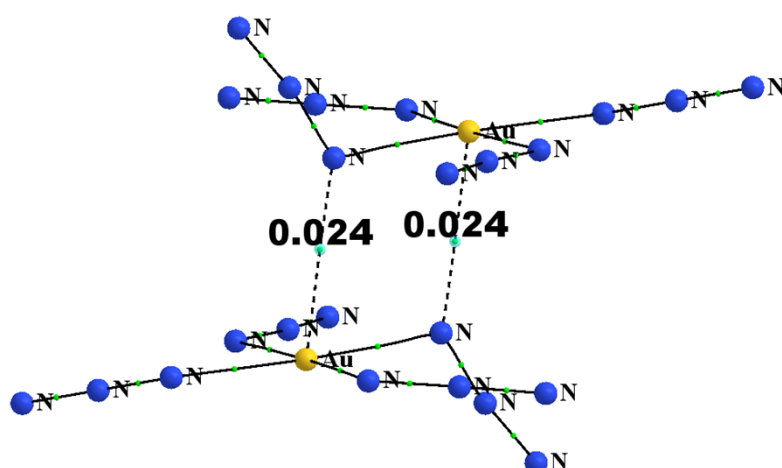


Fig S2. AIM diagram of the $[\text{Au}(\text{N}_3)_4]_2^{2-}$ metastable complex. Densities in au.

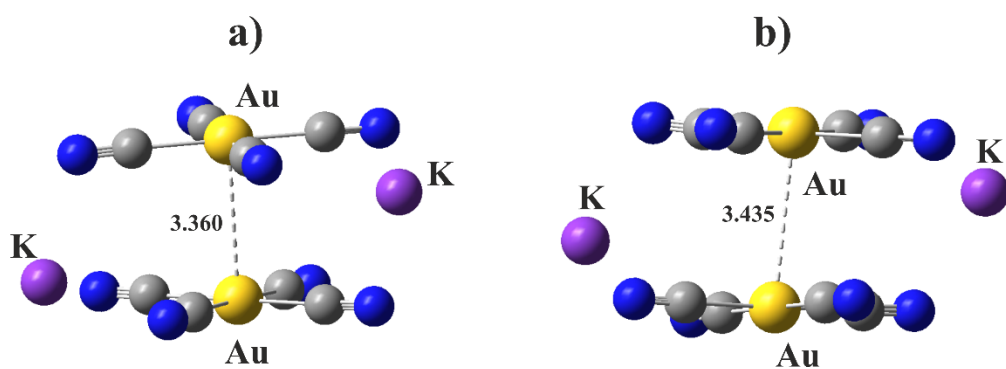


Fig S3. The $\text{K}_2[\text{Au}(\text{N}_3)_4]_2$ complexes formed from dimer I (a) and II (b). Distances in Å.

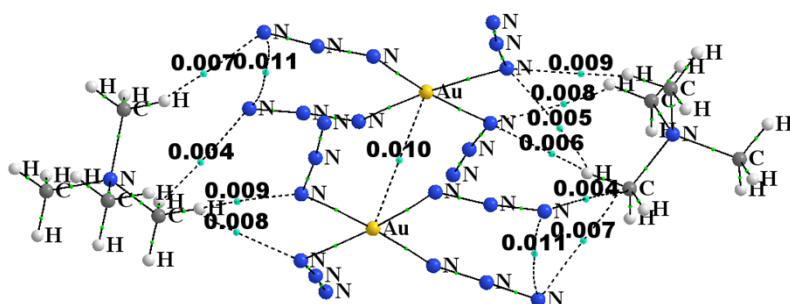


Fig S4. AIM diagram of complex containing a pair of $(\text{NMe}_4)^+$ counterions. Densities in au.

Table S3. ALMO-EDA decomposition of interaction energies (kcal/mol). ELEC= electrostatic term, PAULI = Pauli repulsion, DISP = dispersion, POL = polarization, CT = charge transfer. Percentage contributions are listed as fraction of sum of attractive elements.

complex	ES [%]	POL [%]	CT [%]	DISP [%]	CT ^a , e
K ₂ [Au(CN) ₄] ₂ (I)	53	18	6	23	0.024
K ₂ [Au(CN) ₄] ₂ (II)	54	19	6	22	0.024
[Me ₄ N] ₂ [Au(N ₃) ₄] ₂	43	14	5	38	0.014

^atotal charge transferred from Au species to counterion, as measured by sum of NBO atomic charges

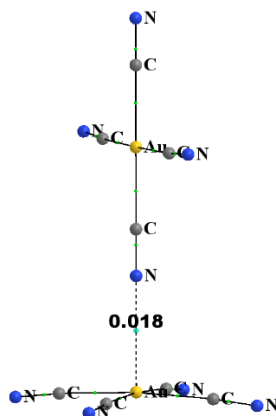


Fig S5. AIM diagram of T-shaped metastable [Au(CN)₄]⁻ complex. Densities in au.

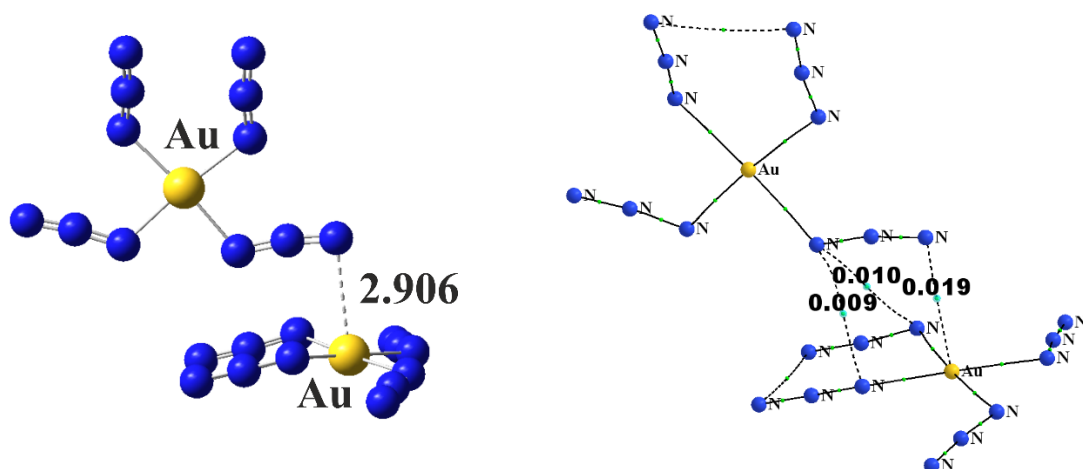


Fig S6. MP2/LANL2DZ/aug-cc-pVDZ optimized structure and AIM diagram of the T-shaped metastable [Au(N₃)₄]₂²⁻ complex. Densities in au, distances in Å.

Coordinates

Trimer $[\text{Au}(\text{CN})_4]_3^{3-}$	Au	2.43050000	6.00160000	7.44280000
	N	2.39980000	7.24820000	4.54900000
	N	2.37980000	8.90690000	8.64890000
	N	2.49770000	4.72310000	10.32370000
	N	2.55560000	3.06920000	6.28600000
	C	2.42980000	6.79710000	5.60980000
	C	2.37980000	7.85440000	8.22360000
	C	2.46970000	5.19570000	9.28200000
	C	2.49770000	4.14560000	6.69210000
	Au	5.77940000	5.87730000	7.68910000
	N	5.54690000	8.65870000	6.24060000
	N	5.68870000	7.31260000	10.48380000
	N	6.11230000	3.08830000	9.08610000
	N	5.81460000	4.52980000	4.85010000
	C	5.62280000	7.65150000	6.77570000
	C	5.72670000	6.79950000	9.48270000
	C	5.97850000	4.10260000	8.57720000
	C	5.81460000	5.01430000	5.88460000
	Au	9.21150000	5.90350000	7.83800000
	N	8.82180000	9.02860000	8.10170000
	N	9.08760000	5.62290000	10.95440000
	N	9.71500000	2.80910000	7.61910000
	N	9.39130000	6.14080000	4.70190000
	C	8.90780000	7.89490000	7.98230000
	C	9.13350000	5.73030000	9.81480000
	C	9.53720000	3.94270000	7.69560000
	C	9.27740000	6.04770000	5.84160000
dimer I $[\text{Au}(\text{CN})_4]_2^{2-}$	Au	2.43050000	6.00160000	7.44280000
	N	2.39980000	7.24820000	4.54900000
	N	2.37980000	8.90690000	8.64890000
	N	2.49770000	4.72310000	10.32370000
	N	2.55560000	3.06920000	6.28600000
	C	2.42980000	6.79710000	5.60980000
	C	2.37980000	7.85440000	8.22360000
	C	2.46970000	5.19570000	9.28200000
	C	2.49770000	4.14560000	6.69210000
	Au	5.77940000	5.87730000	7.68910000
	N	5.54690000	8.65870000	6.24060000
	N	5.68870000	7.31260000	10.48380000
	N	6.11230000	3.08830000	9.08610000
	N	5.81460000	4.52980000	4.85010000
	C	5.62280000	7.65150000	6.77570000
	C	5.72670000	6.79950000	9.48270000
dimer II $[\text{Au}(\text{CN})_4]_2^{2-}$	C	5.97850000	4.10260000	8.57720000
	C	5.81460000	5.01430000	5.88460000
	Au	5.77940000	5.87730000	7.68910000
	N	5.54690000	8.65870000	6.24060000
	N	5.68870000	7.31260000	10.48380000
	N	6.11230000	3.08830000	9.08610000
	N	5.81460000	4.52980000	4.85010000
	C	5.62280000	7.65150000	6.77570000
	C	5.72670000	6.79950000	9.48270000
	C	5.97850000	4.10260000	8.57720000

	C	5.97850000	4.10260000	8.57720000
	C	5.81460000	5.01430000	5.88460000
	Au	9.21150000	5.90350000	7.83800000
	N	8.82180000	9.02860000	8.10170000
	N	9.08760000	5.62290000	10.95440000
	N	9.71500000	2.80910000	7.61910000
	N	9.39130000	6.14080000	4.70190000
	C	8.90780000	7.89490000	7.98230000
	C	9.13350000	5.73030000	9.81480000
	C	9.53720000	3.94270000	7.69560000
	C	9.27740000	6.04770000	5.84160000
Dimer III [Au(N ₃) ₄] ₂ ²⁻	Au	5.17210000	-0.27970000	5.13130000
	N	3.26740000	-0.93200000	5.03800000
	N	7.19460000	0.15790000	5.22740000
	N	7.52660000	1.23590000	4.84180000
	N	3.85100000	2.24820000	5.14210000
	N	2.33410000	-0.18960000	5.07450000
	N	4.87190000	1.67590000	4.86750000
	N	5.76930000	-2.21110000	5.38020000
	N	4.94290000	-3.08070000	5.20570000
	N	1.34980000	0.40020000	5.07180000
	N	4.23170000	-3.96900000	5.04610000
	N	7.93620000	2.26730000	4.49010000
	N	2.89630000	2.86610000	5.38430000
	Au	4.52530000	-0.11600000	1.68820000
	N	6.42840000	0.30410000	1.75600000
	N	7.32220000	-0.47740000	1.85880000
	N	5.63640000	-2.72520000	1.98190000
	N	4.16780000	1.85330000	1.27840000
	N	2.02770000	-1.38700000	1.82360000
	N	5.13080000	2.60420000	1.25000000
	N	2.47150000	-0.25270000	1.61260000
	N	4.60750000	-2.10110000	2.05770000
	N	8.25410000	-1.12700000	1.96840000
	N	1.50480000	-2.36750000	2.03330000
	N	6.53020000	-3.46990000	1.92100000
	N	5.98210000	3.36710000	1.21620000
Dimer III + counterions {[Me ₄ N][Au(N ₃) ₄]} ₂	Au	5.17210000	-0.27970000	5.13130000
	N	3.26740000	-0.93200000	5.03800000
	N	7.19460000	0.15790000	5.22740000
	N	7.52660000	1.23590000	4.84180000
	N	3.85100000	2.24820000	5.14210000
	N	2.33410000	-0.18960000	5.07450000
	N	4.87190000	1.67590000	4.86750000
	N	5.76930000	-2.21110000	5.38020000
	N	4.94290000	-3.08070000	5.20570000
	N	1.34980000	0.40020000	5.07180000
	N	4.23170000	-3.96900000	5.04610000
	N	7.93620000	2.26730000	4.49010000
	N	2.89630000	2.86610000	5.38430000
	Au	4.52530000	-0.11600000	1.68820000
	N	6.42840000	0.30410000	1.75600000
	N	7.32220000	-0.47740000	1.85880000
	N	5.63640000	-2.72520000	1.98190000
	N	4.16780000	1.85330000	1.27840000
	N	2.02770000	-1.38700000	1.82360000
	N	5.13080000	2.60420000	1.25000000
	N	2.47150000	-0.25270000	1.61260000
	N	4.60750000	-2.10110000	2.05770000
	N	8.25410000	-1.12700000	1.96840000

	N	1.50480000	-2.36750000	2.03330000
	N	6.53020000	-3.46990000	1.92100000
	N	5.98210000	3.36710000	1.21620000
	N	9.61140000	-3.75390000	5.18810000
	C	9.04020000	-4.50090000	6.33400000
	H	8.08200000	-4.43900000	6.31100000
	H	9.36470000	-4.12320000	7.15520000
	H	9.30380000	-5.42200000	6.27990000
	C	11.10340000	-3.88590000	5.24900000
	H	11.42710000	-3.48090000	6.05670000
	H	11.49500000	-3.44510000	4.49010000
	H	11.34380000	-4.81520000	5.23820000
	C	9.13770000	-4.35730000	3.90290000
	H	8.18120000	-4.29870000	3.85560000
	H	9.40390000	-5.27910000	3.86510000
	H	9.52540000	-3.88210000	3.16430000
	C	9.24270000	-2.32590000	5.26250000
	H	8.28750000	-2.24020000	5.23140000
	H	9.63040000	-1.85520000	4.52120000
	H	9.57030000	-1.95410000	6.08510000
	N	0.34410000	3.09390000	1.57200000
	C	1.17000000	3.04070000	2.81800000
	H	0.59960000	2.88530000	3.57420000
	H	1.63200000	3.87410000	2.93160000
	H	1.80960000	2.32760000	2.74760000
	C	1.22000000	3.35410000	0.36930000
	H	0.67480000	3.40230000	-0.41940000
	H	1.85520000	2.64050000	0.27600000
	H	1.68680000	4.18410000	0.48840000
	C	-0.33870000	1.79020000	1.40830000
	H	-0.92030000	1.63760000	2.15640000
	H	0.31650000	1.08990000	1.36370000
	H	-0.85500000	1.79830000	0.59930000
	C	-0.68900000	4.18430000	1.71810000
	H	-1.25050000	3.99440000	2.47430000
	H	-1.22540000	4.22640000	0.92400000
	H	-0.24850000	5.02730000	1.85200000
metastable dimer [Au(CN) ₄] ₂ ²⁻	Au	3.04553900	0.00004000	0.00021700
	N	3.27601600	-2.26798900	2.29234700
	N	3.27917900	-2.27193300	-2.28769000
	N	3.27848800	2.26809700	-2.29164700
	N	3.27548500	2.27204100	2.28846200
	C	3.14784200	-1.45031700	1.46034600
	C	3.14985100	-1.45284200	-1.45726500
	C	3.14942800	1.45041100	-1.45979700
	C	3.14747100	1.45293400	1.45785000
	Au	-3.09953700	-0.00004400	-0.00025600
	N	-3.20516700	-3.22747700	-0.00037900
	N	-6.33242200	0.00024200	0.00122300
	N	-3.20492900	3.22738300	-0.00045700
	N	0.12974200	-0.00034100	-0.00152000
	C	-3.13019100	-2.05655800	-0.00028500
	C	-5.15900600	0.00012900	0.00056000
	C	-3.13002600	2.05645900	-0.00032500
	C	-1.04351900	-0.00019000	-0.00096400
metastable dimer III [Au(N ₃) ₄] ₂ ²⁻ (Fig. 4)	Au	1.86910800	0.34870100	0.01621600
	N	2.39026300	-1.52126400	0.62489300
	N	1.45531600	2.22899800	-0.67931300
	N	0.66735300	2.90728800	-0.00936900
	N	0.67958400	0.88229700	2.52365000

	N	1.81923400	-1.96631400	1.62798800
	N	0.38246400	0.49169900	1.38827300
	N	3.27069600	0.21166400	-1.47246400
	N	4.09240000	-0.70464900	-1.41836500
	N	1.35953200	-2.52915100	2.56320900
	N	4.94103000	-1.53098300	-1.49094600
	N	-0.07348600	3.66765400	0.51967500
	N	0.80862300	1.23536400	3.64696700
	Au	-1.86922800	-0.34864200	-0.01622500
	N	-2.39093900	1.52071300	-0.62626500
	N	-1.81846000	1.96611700	-1.62837500
	N	-0.67958300	-0.88235900	-2.52356800
	N	-3.27096400	-0.21099900	1.47225100
	N	-0.66829300	-2.90760900	0.01010600
	N	-4.09262400	0.70532700	1.41777100
	N	-1.45502800	-2.22839500	0.68056000
	N	-0.38241200	-0.49225800	-1.38803100
	N	-1.35748500	2.52914700	-2.56285000
	N	0.07138900	-3.66882500	-0.51933600
	N	-0.80869100	-1.23494700	-3.64702600
	N	-4.94128700	1.53167000	1.48983400
metastable dimer III [Au(N ₃) ₄] ₂ ²⁻ (Fig. S5)	Au	3.35314600	-0.39563500	7.03210400
	N	2.93848000	-0.59915300	9.02563700
	N	3.92742200	-0.35199300	5.07635500
	N	3.10291300	0.06190100	4.25599900
	N	0.77416500	0.85829600	7.21156700
	N	2.19406600	0.18762200	9.61553400
	N	1.51931100	0.25603900	6.43344500
	N	5.23137800	-1.11952300	7.41864600
	N	5.53922700	-1.33782600	8.59125300
	N	1.50120000	0.85839400	10.30927500
	N	5.96618300	-1.59361000	9.66875000
	N	2.44890700	0.42396900	3.33639000
	N	-0.04416400	1.44909600	7.83567400
	Au	4.62157700	0.01768700	1.45025600
	N	5.57633400	1.13120700	2.86255300
	N	6.41037300	0.60212400	3.60659600
	N	5.58803400	-2.02849900	3.20231500
	N	4.43403100	1.74724100	0.33495300
	N	3.50168300	-2.15542100	-0.03794200
	N	5.04794600	2.74708400	0.70440700
	N	3.59448300	-0.92947900	-0.07278200
	N	4.66501000	-1.77226800	2.42042600
	N	7.22106400	0.23162100	4.38745200
	N	3.34452100	-3.33112300	-0.11084600
	N	6.39842200	-2.40432100	3.98093200
	N	5.58892700	3.77317400	0.96237700