Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Azido-mediated intermolecular interactions of transition metal complexes

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SUPPORTING INFORMATION

Table S1. Cartesian coordinates of gas phase optimized dimers of [N_3-Hg(CF_3)] with different topologies and torsion angles τ.

1a

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.1237490
N	0.1049310	0.0000000	2.3363450
Hg	-1.5312370	-0.0009390	3.5517280
C	-3.1160370	-0.0024880	4.9223830
F	-2.6955320	-0.2422630	6.1713440
F	-4.0273340	-0.9395310	4.6311360
F	-3.7595580	1.1716150	4.9467080
N	3.1554860	0.0016580	2.0723670
N	3.2604170	0.0016580	3.2849630
N	3.2604170	0.0015530	4.4087120
Hg	4.7916540	0.0025970	0.8569840
C	6.3764540	0.0028860	-0.5136710
F	5.9562080	-0.2372270	-1.7626540
F	7.2887610	-0.9332010	-0.2225120
F	7.0187090	1.1776840	-0.5378870

1b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.1237490
N	0.1049310	0.0000000	2.3363450
Hg	-1.5312370	-0.0009390	3.5517280
C	-3.1160370	-0.0024880	4.9223830
F	-2.6955320	-0.2422630	6.1713440
F	-4.0273340	-0.9395310	4.6311360
F	-3.7595580	1.1716150	4.9467080
N	3.1757440	0.0016690	2.0706140
N	3.2806750	0.0016690	3.2832100
N	3.3773000	-0.0952120	4.3985970
Hg	3.0825780	1.7365260	1.0048780
C	2.9763430	3.4335930	-0.2194440
F	3.1051610	3.1225890	-1.5159410
F	3.9407330	4.3174020	0.0672080
F	1.8086120	4.0755440	-0.0870340

2a

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.1237490
N	0.1049310	0.0000000	2.3363450
Hg	-1.5312370	-0.0009390	3.5517280
C	-3.1160370	-0.0024880	4.9223830
F	-2.6955310	-0.2422630	6.1713440
F	-4.0273340	-0.9395310	4.6311360

F	-3.7595580	1.1716150	4.9467080
N	2.4343730	0.0011800	3.9707280
N	3.0897930	0.0015820	2.9451430
N	1.7498560	0.0007170	4.8619330
Hg	5.1277160	0.0026790	2.9779160
C	7.2194820	0.0031830	2.8562580
F	7.6470210	-0.2364720	1.6096640
F	7.7657230	-0.9331240	3.6425690
F	7.7434840	1.1779000	3.2286710

2b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.1237490
N	0.1049310	0.0000000	2.3363450
Hg	-1.5312370	-0.0009390	3.5517280
C	-3.1160360	-0.0024880	4.9223830
F	-2.6955310	-0.2422630	6.1713440
F	-4.0273330	-0.9395310	4.6311360
F	-3.7595580	1.1716150	4.9467090
N	2.4161850	0.0011710	3.9579660
N	3.1152680	0.0015950	2.9616310
N	1.7732350	-0.0960990	4.8744620
Hg	3.7287940	1.7368240	2.0859790
C	4.4342520	3.4343190	1.0804310
F	5.3663550	3.1237300	0.1699700
F	4.9886570	4.3178810	1.9202460
F	3.4545600	4.0764080	0.4314660

3b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	0.0497490	0.0002120	5.7997540
N	1.2667640	-0.0005310	5.8163180
N	2.3862830	0.0956670	5.8316010
Hg	-1.0210120	-1.7339930	5.7852870
C	-2.2508660	-3.4303090	5.7692830
F	-3.5343860	-3.1183790	5.9917610
F	-1.8954580	-4.3137790	6.7108260
F	-2.2040350	-4.0729860	4.5954000

4a

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.0418740	-0.0016470	1.0857600
N	2.9900630	1.2143760	1.0879410
N	2.9928270	-1.1243220	1.0878780
Hg	4.6761920	2.3571200	1.0150690
C	6.3177980	3.6572310	0.9434820
F	5.9423730	4.9233650	0.7194690
F	7.1747630	3.3264290	-0.0309490
F	7.0112070	3.6534480	2.0890820

4b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	2.9331320	-0.0015880	1.0904560
N	2.9315500	1.2144050	1.0379330
N	2.9304610	-1.1242910	1.0420670
Hg	3.0049830	2.3581010	2.7233920
C	3.0772090	3.6591390	4.3642360
F	3.3018460	4.9249420	3.9880690
F	4.0514770	3.3283590	5.2213960
F	1.9316070	3.6563260	5.0576460

5a

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	0.1876480	0.0001070	5.4073740
N	-1.0293670	0.0008570	5.3908110

N	1.3084270	-0.0005300	5.3257380
Hg	-2.1226770	0.0014990	7.1109490
C	-3.3745800	0.0028680	8.7911350
F	-4.6506430	0.2436050	8.4626070
F	-3.0173310	0.9391960	9.6793910
F	-3.3528070	-1.1716080	9.4340650

5b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	0.3195400	0.0000260	5.3924600
N	-0.8897830	0.1057000	5.4806090
N	1.4403190	-0.0006640	5.3108240
Hg	-2.1029590	-1.5297230	5.5689240
C	-3.4709180	-3.1136820	5.6691560
F	-4.6988850	-2.6925560	5.9992650
F	-3.1129670	-4.0257240	6.5820560
F	-3.5808950	-3.7564770	4.4995630

6a

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.2235140	-0.0019250	2.0661310
N	3.3203950	-0.0019250	3.1856960
N	3.3203950	-0.0017960	4.4028240
Hg	5.0552530	-0.0028600	5.4726240
C	6.7523190	-0.0032520	6.7015460
F	6.4413480	0.2370380	7.9820850
F	7.6362570	0.9326740	6.3327200
F	7.3941090	-1.1781420	6.6704260

6b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930

Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.2182670	-0.0019220	2.0665850
N	3.3151480	-0.0019220	3.1861500
N	3.4198160	0.1030100	4.3942200
Hg	3.5298840	-1.5331520	5.6046190
C	3.6538690	-3.1179420	6.9696660
F	3.9997950	-2.6968550	8.1932840
F	4.5644040	-4.0269560	6.5982400
F	2.4878390	-3.7643190	7.0953570

7a

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.1612120	-0.0017110	0.0000000
N	3.1612120	-0.0017110	1.2171280
N	3.0643310	-0.0016070	-1.1195650
Hg	4.8960690	-0.0026510	2.2869280
C	6.5931360	-0.0029390	3.5158510
F	6.2821320	0.2371730	4.7964150
F	7.4769450	0.9331470	3.1471230
F	7.2350870	-1.1777380	3.4846060

7b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.0667150	-0.0016600	0.0000000
N	3.0667140	-0.0016600	1.2171280
N	3.0668190	0.0952200	-1.1195650
Hg	3.0657750	-1.7365180	2.2869280
C	3.0654860	-3.4335850	3.5158510
F	3.3055990	-3.1225810	4.7964140
F	4.0015730	-4.3173940	3.1471230

F	1.8906880	-4.0755350	3.4846060

8b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.7706180	-0.0887440	0.9358550
N	3.8215330	-0.0545680	2.1514380
N	3.7251170	-0.0233480	-0.1850660
Hg	3.8433540	-1.7585230	3.2695900
C	3.8729600	-3.4202470	4.5455540
F	4.1703550	-3.0767660	5.8056330
F	4.7815230	-4.3269490	4.1637940
F	2.6898390	-4.0464790	4.5814320

9b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.1417300	-0.0019340	0.9452600
N	3.2386110	-0.0019340	2.0648250
N	3.3432800	0.1029970	3.2728950
Hg	3.4469970	-1.5331710	4.4838450
C	3.5647700	-3.1179710	5.8494310
F	3.9118420	-2.6977610	7.0730260
F	4.4721010	-4.0304170	5.4785810
F	2.3963500	-3.7600520	5.9749560

Table S2. Cartesian coordinates of dimers of [N_3-Hg(CF_3)] optimized in water with different topologies and torsion angles τ.

1a

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.1237490
N	0.1049310	0.0000000	2.3363450
Hg	-1.5312370	-0.0009390	3.5517280

C	-3.1160370	-0.0024880	4.9223830
F	-2.6955320	-0.2422630	6.1713440
F	-4.0273340	-0.9395310	4.6311360
F	-3.7595580	1.1716150	4.9467080
N	4.0691430	0.0021540	1.9933040
N	4.1740750	0.0021540	3.2059010
N	4.1740750	0.0020490	4.3296490
Hg	5.7053120	0.0030930	0.7779210
C	7.2901120	0.0033820	-0.5927340
F	6.8698660	-0.2367300	-1.8417170
F	8.2024190	-0.9327050	-0.3015740
F	7.9323660	1.1781810	-0.6169500

1b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.1237490
N	0.1049310	0.0000000	2.3363450
Hg	-1.5312370	-0.0009390	3.5517280
C	-3.1160370	-0.0024880	4.9223830
F	-2.6955320	-0.2422630	6.1713440
F	-4.0273340	-0.9395310	4.6311360
F	-3.7595580	1.1716150	4.9467080
N	4.0131480	0.0021240	1.9981500
N	4.1180790	0.0021240	3.2107460
N	4.2147040	-0.0947570	4.3261330
Hg	3.9199820	1.7369810	0.9324140
C	3.8137460	3.4340480	-0.2919080
F	3.9425640	3.1230440	-1.5884050
F	4.7781370	4.3178570	-0.0052560
F	2.6460150	4.0759990	-0.1594980

2a

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.1237490
N	0.1049310	0.0000000	2.3363450
Hg	-1.5312370	-0.0009390	3.5517280
C	-3.1160370	-0.0024880	4.9223830
F	-2.6955310	-0.2422630	6.1713440
F	-4.0273340	-0.9395310	4.6311360
F	-3.7595580	1.1716150	4.9467080
N	3.2880590	0.0016130	4.5696910
N	3.9434790	0.0020140	3.5441060
N	2.6035420	0.0011490	5.4608970
Hg	5.9814010	0.0031120	3.5768790
C	8.0731670	0.0036160	3.4552210
F	8.5007070	-0.2360390	2.2086270
F	8.6194080	-0.9326910	4.2415330
F	8.5971700	1.1783320	3.8276340

2b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.1237490
N	0.1049310	0.0000000	2.3363450
Hg	-1.5312370	-0.0009390	3.5517280
C	-3.1160360	-0.0024880	4.9223830
F	-2.6955310	-0.2422630	6.1713440
F	-4.0273330	-0.9395310	4.6311360
F	-3.7595580	1.1716150	4.9467090
N	2.7515360	0.0013410	4.1932550
N	3.4506190	0.0017640	3.1969200
N	2.1085850	-0.0959300	5.1097510
Hg	4.0641450	1.7369940	2.3212680
C	4.7696030	3.4344890	1.3157190
F	5.7017060	3.1239000	0.4052580
F	5.3240080	4.3180510	2.1555350
F	3.7899110	4.0765770	0.6667550

3b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	0.0418960	0.0002470	6.3767800
N	1.2589110	-0.0004960	6.3933430
N	2.3784300	0.0957020	6.4086270
Hg	-1.0288650	-1.7339570	6.3623130
C	-2.2587200	-3.4302740	6.3463090
F	-3.5422400	-3.1183440	6.5687870
F	-1.9033120	-4.3137430	7.2878520
F	-2.2118880	-4.0729510	5.1724260

4a

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.0809460	-0.0016680	1.0840730

N	3.0291350	1.2143550	1.0862530
N	3.0318990	-1.1243440	1.0861910
Hg	4.7152640	2.3570990	1.0133820
C	6.3568710	3.6572100	0.9417950
F	5.9814450	4.9233440	0.7177820
F	7.2138350	3.3264080	-0.0326370
F	7.0502790	3.6534270	2.0873950

4b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.0453890	-0.0016490	1.0856080
N	3.0438070	1.2143440	1.0330850
N	3.0427180	-1.1243520	1.0372190
Hg	3.1172400	2.3580400	2.7185440
C	3.1894660	3.6590780	4.3593880
F	3.4141030	4.9248810	3.9832210
F	4.1637340	3.3282980	5.2165480
F	2.0438640	3.6562650	5.0527980

5a

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	0.2117290	0.0001350	6.2220500
N	-1.0052860	0.0008860	6.2054870
N	1.3325080	-0.0005010	6.1404140
Hg	-2.0985960	0.0015270	7.9256250
C	-3.3504990	0.0028970	9.6058110
F	-4.6265620	0.2436330	9.2772830
F	-2.9932490	0.9392250	10.4940670
F	-3.3287260	-1.1715800	10.2487410

5b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280

N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	0.3747500	0.0000320	6.1501540
N	-0.8345730	0.1057070	6.2383030
N	1.4955290	-0.0006570	6.0685180
Hg	-2.0477490	-1.5297160	6.3266190
C	-3.4157090	-3.1136750	6.4268500
F	-4.6436750	-2.6925500	6.7569590
F	-3.0577570	-4.0257180	7.3397500
F	-3.5256860	-3.7564710	5.2572570

6a

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.4343620	-0.0020550	2.0478860
N	3.5312430	-0.0020550	3.1674500
N	3.5312430	-0.0019260	4.3845780
Hg	5.2661000	-0.0029880	5.4543780
C	6.9631670	-0.0033780	6.6833010
F	6.6521960	0.2369120	7.9638390
F	7.8471040	0.9325490	6.3144750
F	7.6049580	-1.1782670	6.6521810

6b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.4736020	-0.0020790	2.0444900
N	3.5704830	-0.0020790	3.1640550
N	3.6751520	0.1028520	4.3721250
Hg	3.7892570	-1.5332920	5.5821730
C	3.9171920	-3.1180650	6.9468760
F	4.2623870	-2.6964220	8.1705090

F	4.8297570	-4.0248900	6.5750840
F	2.7526890	-3.7671690	7.0726710

7a

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.9498140	-0.0021380	0.0000000
N	3.9498140	-0.0021380	1.2171280
N	3.8529330	-0.0020340	-1.1195650
Hg	5.6846720	-0.0030780	2.2869280
C	7.3817380	-0.0033660	3.5158510
F	7.0707340	0.2367460	4.7964150
F	8.2655480	0.9327200	3.1471230
F	8.0236890	-1.1781650	3.4846060

7b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.2791130	-0.0017750	0.0000000
N	3.2791130	-0.0017750	1.2171280
N	3.2792180	0.0951050	-1.1195650
Hg	3.2781740	-1.7366330	2.2869280
C	3.2778850	-3.4337000	3.5158510
F	3.5179970	-3.1226960	4.7964140
F	4.2139720	-4.3175090	3.1471230
F	2.1030860	-4.0756500	3.4846060

8b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950

F	-4.0751460	-1.1716150	-2.2674780
N	4.0577170	-0.0955010	0.9144390
N	4.1086320	-0.0613250	2.1300210
N	4.0122730	-0.0301060	-0.2064840
Hg	4.1294410	-1.7652650	3.2482160
C	4.1580580	-3.4269750	4.5242210
F	4.4556320	-3.0836370	5.7842960
F	5.0660980	-4.3342160	4.1424980
F	2.9745710	-4.0525160	4.5600940

9b

N	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.2171280
N	0.0968810	0.0000000	2.3366930
Hg	-1.7348580	0.0009390	-1.0698000
C	-3.4319240	0.0024880	-2.2987230
F	-3.1206600	0.2422630	-3.5792860
F	-4.3147190	0.9395310	-1.9299950
F	-4.0751460	-1.1716150	-2.2674780
N	3.7998320	-0.0023390	0.8883120
N	3.8967130	-0.0023390	2.0078760
N	4.0013820	0.1025920	3.2159470
Hg	4.1050990	-1.5335770	4.4268970
C	4.2228720	-3.1183770	5.7924830
F	4.5699440	-2.6981660	7.0160780
F	5.1302030	-4.0308220	5.4216320
F	3.0544520	-3.7604570	5.9180070

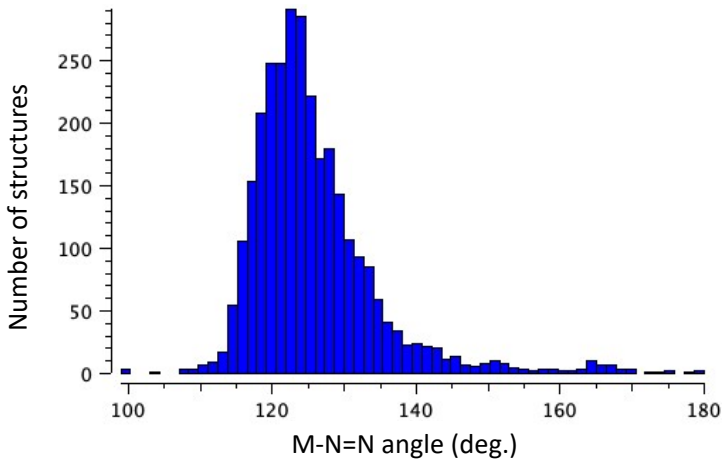


Figure S1. Histogram of the distribution of M-N-N angles in azido-containing transition metal complexes as found in the CSD.

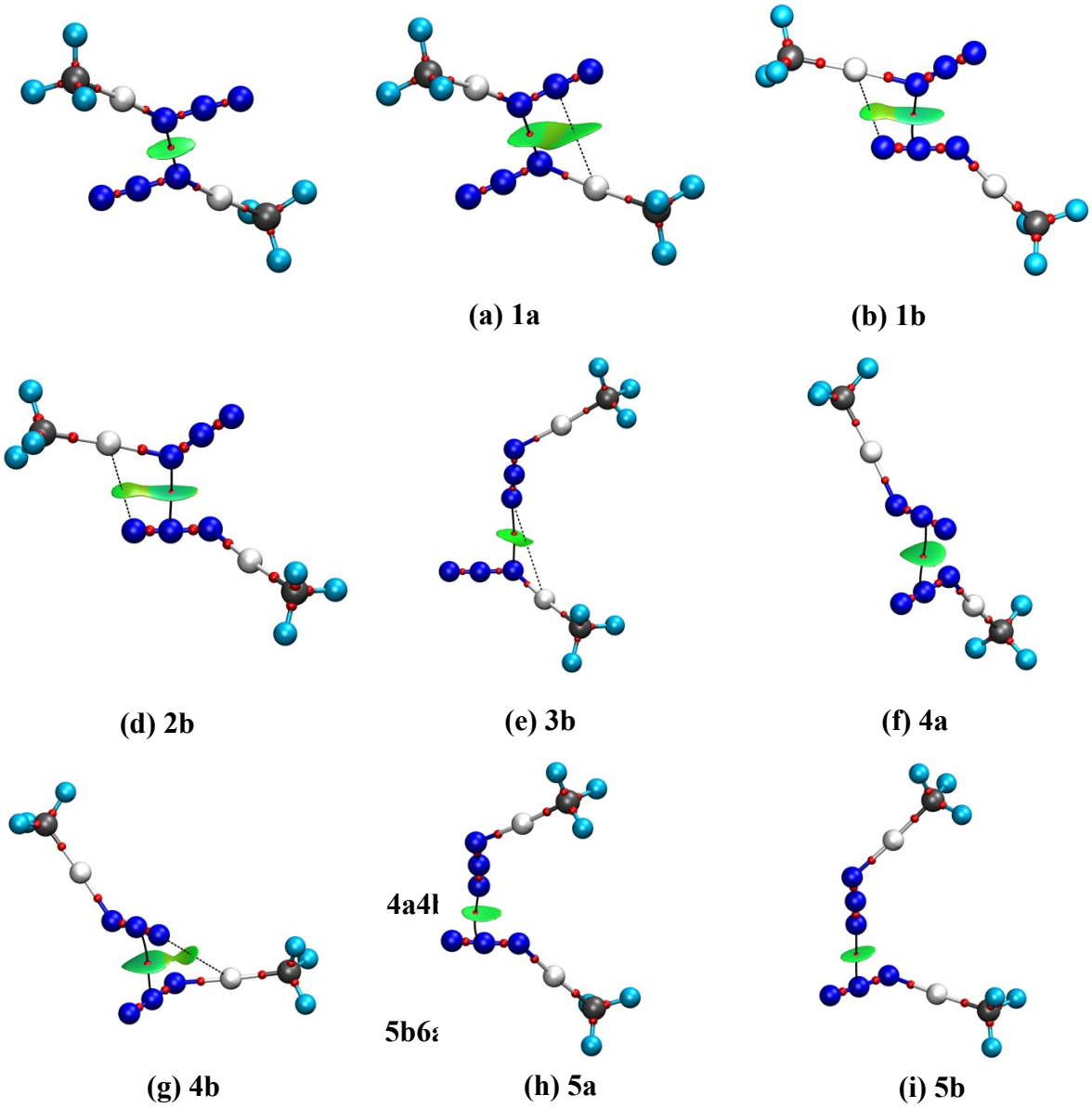
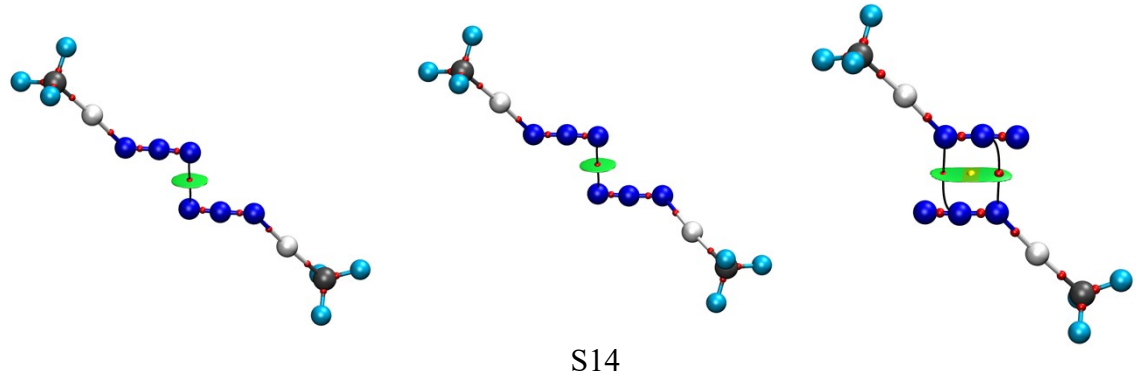


Figure S2. Molecular graphs and NCI isosurfaces (s = 0.4) of dimers of [N_3-Hg(CF_3)] with different topologies and torsion angles τ. For each topology, model **a** has a dihedral angle τ of 180° and model **b** corresponds to τ = 90°. The isosurfaces are coloured according to a BRG scheme from -0.035 < sign(λ_2)ρ < 0.030 a.u. Small spheres represent BCPs (red) and RCPs (yellow). The solid lines represent the azido···azido BP and the dashed lines indicate the secondary N···Hg contact.



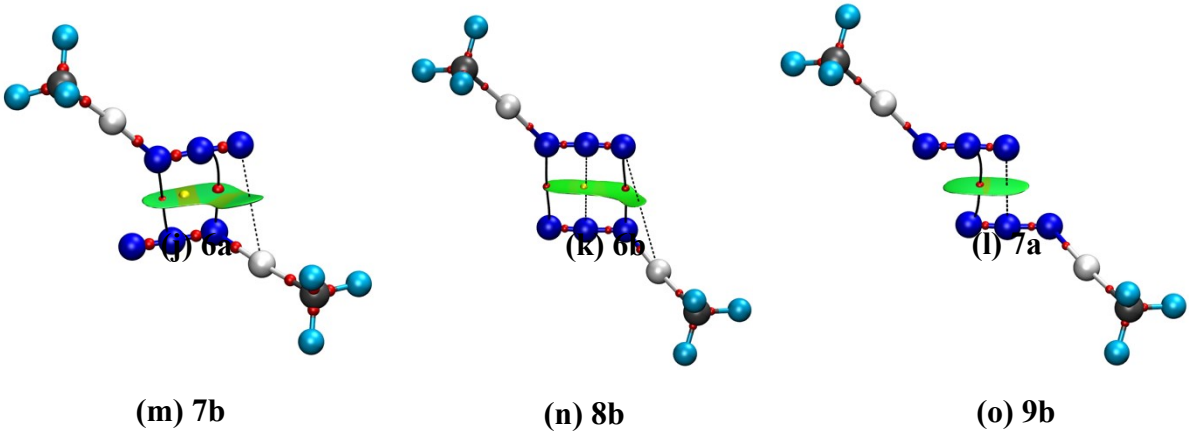


Figure S3. Molecular graphs and NCI isosurfaces (s = 0.4) of dimers of [N_3-Hg(CF_3)] with different topologies and torsion angles τ. For each topology, model **a** has a dihedral angle τ of 180° and model **b** corresponds to τ = 90°. The isosurfaces are coloured according to a BRG scheme from -0.035 < sign(λ_2)ρ < 0.030 a.u. Small spheres represent BCPs (red) and RCPs (yellow). The solid lines represent the azido···azido BP and the dashed lines indicate the secondary N···Hg contact. (continuation)

Exponential least-squares fittings equations for Figure 5.

a) Pauli = $1.58 \cdot e^{(-0.446 \cdot \text{Elec})}$ ($R^2 = 0.65$) [Eq. A3.1]

Exponential least-squares fittings equations for Figure 6.

a) $\rho_{BCP} = 0.0047 \cdot e^{(0.032 \cdot \%p_{N \cdot\cdot N})}$ ($R^2 = 0.85$) [Eq. A4.2]

b) $\nabla^2\rho_{BCP} = 0.0184 \cdot e^{(0.039 \cdot \%p_{N \cdot\cdot N})}$ ($R^2 = 0.99$) [Eq. A4.3]

c) $|V_{BCP}| = 7.44 \cdot e^{(-2.41 \cdot \%p_{N \cdot\cdot N})}$ ($R^2 = 0.95$) [Eq. A4.4]

d) $G_{BCP} = 0.0036 \cdot e^{(0.042 \cdot \%p_{N \cdot\cdot N})}$ ($R^2 = 0.98$) [Eq. A4.5]

Table S3. Key geometrical parameters including distances in Å, penetrations (pen.) in % and interaction energies (kcal/mol) for all studied interaction topologies of the [N_3-Hg(CF_3)] dimers, optimized at the M06-2X/def2-TZVP level in the presence of water as the solvent.

Compd.	ϕ (°)	N contact	N···N	pen.	N-Hg cont.	N···Hg[b]	pen.	ΔEINT
1a	180	Nα···Nα	3.979	-35				-0.47
2a	180	Nα···Nβ	3.888	-30	Nγ···Hg	4.554	-21	-0.89
4a	180	Nβ···Nβ	3.084	12				-0.90
5a	180	Nγ···Nβ	3.887	-30				0.07

6a	180	$N_\gamma\cdots N_\gamma$	3.350	-2				-0.19
7a	180	$N_\alpha\cdots N_\beta$	3.950	-33				-0.53
		$N_\beta\cdots N_\alpha$	3.950	-33				
1b	90	$N_\alpha\cdots N_\alpha$	3.923	-32	$N_\beta\cdots Hg$	4.292	-9	-1.22
2b	90	$N_\alpha\cdots N_\beta$	3.233	5	$N_\gamma\cdots Hg$	3.960	7	-2.82
3b	90	$N_\gamma\cdots N_\alpha$	4.040	-38	$N_\gamma\cdots Hg$	4.525	-20	-0.54
4b	90	$N_\beta\cdots N_\beta$	3.048	14	$N_\gamma\cdots Hg$	3.851	12	-2.46
5b	90	$N_\gamma\cdots N_\beta$	3.824	-27	$N_\gamma\cdots Hg$	4.781	-32	-0.38
6b	90	$N_\gamma\cdots N_\gamma$	3.389	-4				-0.70
7b	90	$N_\alpha\cdots N_\beta$	3.279	2	$N_\gamma\cdots Hg$	3.625	23	-2.52
		$N_\beta\cdots N_\alpha$	3.279	2				
8b	90	$N_\alpha\cdots N_\gamma$	4.018	-37	$N_\gamma\cdots Hg$	4.495	-19	-0.71
		$N_\beta\cdots N_\beta$	4.070	-39				
		$N_\gamma\cdots N_\alpha$	4.018	-37				
9b	90	$N_\beta\cdots N_\gamma$	3.814	-26	$N_\gamma\cdots Hg$	4.774	-32	-0.65
		$N_\gamma\cdots N_\beta$	3.814	-26				

Table S4. Interaction energies of dimers of [N_3-Hg(CF_3)] with different interaction topologies calculated with different functionals.

		ΔE_{INT}					
Compd.	**Φ (°)**	**M062X**	**wB97xD**	**BP86-D3**	**B3LYP-D3**	**B2PLYP-D3**	**PBE0-D3**
1a	180	-1.12	-1.74	-1.73	-1.95	-1.95	-2.11
2a	180	-2.74	-2.88	-3.13	-3.34	-3.42	-3.48
4a	180	-0.91	-0.97	-1.06	-1.33	-1.37	-1.47
5a	180	-0.10	-0.12	-0.08	-0.43	-0.55	-0.60
6a	180	-0.21	-0.33	-0.39	-0.65	-0.70	-0.76
7a	180	-1.08	-1.38	-1.28	-1.63	-1.78	-1.93
1b	90	-2.20	-3.31	-3.80	-3.77	-3.40	-3.64
2b	90	-3.71	-4.37	-4.48	-4.59	-4.38	-4.67
3b	90	-0.63	-1.19	-1.04	-1.26	-1.21	-1.38
4b	90	-2.52	-2.68	-2.95	-3.10	-3.05	-3.20
5b	90	-0.59	-0.93	-0.87	-1.18	-1.17	-1.29
6b	90	-0.75	-0.95	-0.96	-1.26	-1.28	-1.37
7b	90	-2.71	-3.21	-3.54	-3.67	-3.59	-3.79
8b	90	-0.75	-1.57	-1.47	-1.63	-1.60	-1.91
9b	90	-0.89	-1.22	-1.29	-1.53	-1.60	-1.73

Table S5. N···N interatomic distances of dimers of [N_3-Hg(CF_3)] with different interaction topologies calculated with different functionals.

			N···N (Å)					
Compd.	**Φ (°)**	**N contact**	**M06-2X**	**wB97xD**	**BP86-D3**	**B3LYP-D3**	**B2PLYP-D3**	**PBE0-D3**
1a	180	$N_\alpha\cdots N_\alpha$	3.062	3.098	3.021	3.045	3.010	3.028
2a	180	$N_\alpha\cdots N_\beta$	2.846	2.986	2.918	2.932	2.881	2.896
4a	180	$N_\beta\cdots N_\beta$	3.045	3.336	3.199	3.183	3.090	3.154
5a	180	$N_\gamma\cdots N_\beta$	3.072	3.362	3.202	3.142	3.078	3.116
6a	180	$N_\gamma\cdots N_\gamma$	3.138	3.379	3.207	3.181	3.111	3.176
7a	180	$N_\alpha\cdots N_\beta$	3.161	3.318	3.247	3.236	3.168	3.207
		$N_\beta\cdots N_\alpha$	3.161	3.318	3.247	3.236	3.168	3.207
1b	90	$N_\alpha\cdots N_\alpha$	3.082	3.219	3.041	3.066	3.036	3.064
2b	90	$N_\alpha\cdots N_\beta$	2.823	2.945	2.859	2.890	2.852	2.863
3b	90	$N_\gamma\cdots N_\alpha$	3.463	3.444	3.289	3.301	3.263	3.311
4b	90	$N_\beta\cdots N_\beta$	2.936	3.148	3.055	3.062	2.997	3.044
5b	90	$N_\gamma\cdots N_\beta$	3.064	3.245	3.118	3.109	3.067	3.100
6b	90	$N_\gamma\cdots N_\gamma$	3.133	3.331	3.184	3.165	3.108	3.160
7b	90	$N_\alpha\cdots N_\beta$	3.067	3.264	3.147	3.157	3.107	3.134
		$N_\beta\cdots N_\alpha$	3.067	3.264	3.147	3.157	3.107	3.134
8b	90	$N_\alpha\cdots N_\gamma$	3.730	3.597	3.412	3.481	3.384	3.481
		$N_\beta\cdots N_\beta$	3.782	3.649	3.464	3.533	3.437	3.533
		$N_\gamma\cdots N_\alpha$	3.730	3.596	3.412	3.481	3.384	3.481
9b	90	$N_\beta\cdots N_\gamma$	3.153	3.416	3.247	3.253	3.174	3.247
		$N_\gamma\cdots N_\beta$	3.153	3.416	3.247	3.253	3.174	3.247

Table S6. N···Hg interatomic distances of dimers of [N_3-Hg(CF_3)] with different interaction topologies calculated with different functionals.

			N-Hg (Å)					
Compd.	**Φ (°)**	**N-Hg cont.**	**M06-2X**	**wB97xD**	**BP86-D3**	**B3LYP-D3**	**B2PLYP-D3**	**PBE0-D3**
2a	180	$N_\gamma\cdots$Hg	3.533	3.670	3.604	3.617	3.568	3.582
1b	90	$N_\beta\cdots$Hg	3.540	3.659	3.505	3.525	3.500	3.524

2b	90	$N_{\gamma}\cdots Hg$	3.561	3.679	3.595	3.626	3.589	3.600
3b	90	$N_{\gamma}\cdots Hg$	4.019	4.002	3.869	3.880	3.847	3.888
4b	90	$N_{\gamma}\cdots Hg$	3.764	3.929	3.856	3.862	3.811	3.847
5b	90	$N\gamma\cdots Hg$	4.198	4.332	4.238	4.232	4.201	4.225
7b	90	$N_{\gamma}\cdots Hg$	3.440	3.611	3.509	3.518	3.474	3.498
8b	90	$N_{\gamma}\cdots Hg$	4.242	4.127	3.969	4.028	3.946	4.028
9b	90	$N_{\gamma}\cdots Hg$	4.264	4.462	4.334	4.339	4.279	4.334