Supporting Information

Metal-involving Bifurcated Halogen Bonding C–Br•••η^2(Cl–Pt)

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Table 1S. Crystal data and structure refinement for **1**•CBr_4•$CHCl_3$, **2**•2CBr_4, and **3**•2CBr_4.

Structure	**1**•CBr_4•$CHCl_3$	**2**•2CBr_4	**3**•2CBr_4
CCDC number	1843328	1843330	1879337
Empirical formula	$C_8H_{13}Br_4Cl_5N_4Pt$	$C_{12}H_{20}Br_8Cl_2N_4Pt$	$C_{12}H_{16}Br_8Cl_2N_4Pt$
Formula weight	857.20	1125.59	1121.47
Temperature/K	100(2)	200(2)	100(2)
Crystal system	triclinic	triclinic	monoclinic
Space group	P-1	P-1	$P2_1$
a/Å	7.9983(6)	8.0320(6)	8.5953(2)
b/Å	8.0773(6)	8.5980(6)	16.2039(3)
c/Å	19.2449(14)	11.6600(7)	10.0203(2)
α/°	79.420(7)	76.646(6)	90
β/°	83.272(6)	88.965(5)	111.979(3)
γ/°	63.302(8)	65.283(7)	90
Volume/Å^3	1091.02(16)	708.87(9)	1294.17(5)
Z	2	1	2
ρ_{calc}g/cm^3	2.609	2.637	2.868
μ/mm^{-1}	14.366	24.273	17.985
F(000)	784.0	512.0	1008.0
Crystal size/mm^3	0.43 × 0.41 × 0.27	0.16 × 0.14 × 0.11	0.15 × 0.14 × 0.1
Radiation	MoKα (λ = 0.7107)	CuKα (λ = 1.5418)	MoKα (λ = 0.7107)
2Θ range for data collection/°	5.706 to 52.994	7.824 to 152.622	5.028 to 55.496
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 9, -23 ≤ l ≤ 24	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -14 ≤ l ≤ 14	-11 ≤ h ≤ 11, -21 ≤ k ≤ 21, -12 ≤ l ≤ 13
Reflections collected	8618	7662	13791
Independent reflections	4509 [R_{int} = 0.0405, R_{sigma} = 0.0655]	2946 [R_{int} = 0.0523, R_{sigma} = 0.0472]	6079 [R_{int} = 0.0345, R_{sigma} = 0.0491]
Data/restraints/parameters	4509/0/206	2946/3/136	6079/1/244
Goodness-of-fit on F^2	1.011	1.039	1.020
Final R indexes [I≥2σ (I)]	R_1 = 0.0378, wR_2 = 0.0720	R_1 = 0.0371, wR_2 = 0.0922	R_1 = 0.0293, wR_2 = 0.0561
Final R indexes [all data]	R_1 = 0.0511, wR_2 = 0.0773	R_1 = 0.0430, wR_2 = 0.0968	R_1 = 0.0336, wR_2 = 0.0574
Largest diff. peak/hole / e·Å^{-3}	2.26/–1.36	1.08/–1.29	1.07/–1.17

Table 2S. Parameters and calculated energies (kcal/mol) of the Br_3C–Br•••Cl–Pt XBs.

Structure	Br_3C–Br•••Cl–Pt	*d*(Br•••Cl), Å	∠(C–Br•••Cl),°	∠(Br•••Cl–Pt),°	E_{int}[b]	E_{int}[c]	$\|E^V_{cont}\|$[d]	$\|E^G_{cont}\|$[e]
1•$CHCl_3$•CBr_4	C1S–Br2S•••Cl1–Pt1	3.350(2)	157.7(3)	79.30(5)	1.9	1.9	2.2	2.5
	C1S–Br4S•••Cl1A–Pt1A	3.0991(15)	173.6(2)	123.93(8)	3.1	3.2	4.0	4.7
	C1S–Br1S•••Cl1A–Pt1A	3.1797(16)	175.9(3)	88.17(5)	2.5	2.7	3.3	3.9
	C1S–Br3S•••Cl1A–Pt1A	3.131(2)	173.2(2)	121.28(7)	2.8	3.0	3.6	4.3
2•2CBr_4	C1S–Br3S•••Cl1–Pt1	3.5254(15)	159.5(2)	135.93(7)	1.3	1.4	1.6	2.0
	C1S–Br1S•••Cl1–Pt1	3.294(2)	173.0(2)	124.68(7)	1.9	2.2	2.8	3.3
	C1S–Br2S•••Cl1–Pt1	3.4685(19)	167.13(17)	77.56(4)	1.6	1.6	1.7	2.1
	C1S–Br4S•••Cl1–Pt1	3.4485(19)	161.18(19)	142.67(7)	1.3	1.6	1.6	2.1
3•2CBr_4	C1S–Br3S•••Cl1–Pt1	3.582(2)	172.0(4)	83.30(7)	1.9	2.2		
	C2S–Br5S•••Cl1–Pt1	3.128(2)	177.0(3)	116.63(9)	2.8	3.0		
	C2S–Br8S•••Cl1–Pt1	3.176(3)	167.3(3)	97.44(9)	2.8	2.7		
	C1S–Br1S•••Cl2–Pt1	3.119(2)	175.6(3)	116.93(9)	2.8	3.0		
	C1S–Br2S•••Cl2–Pt1	3.186(3)	172.8(6)	102.09(9)	2.5	2.7		
	C2S–Br6S•••Cl2–Pt1	3.305(2)	157.2(3)	105.52(6)	1.9	2.2		
	C2S–Br7S•••Cl2–Pt1	3.499(2)	176.1(3)	82.44(6)	1.3	1.3		
	Comparison[a]	*3.6 (Br•••Cl)*	*180*	*90*				

[a] Comparison with the sum of Bondi vdW radii and with the typical XB's angle.
[b] $E_{int} = -V(\mathbf{r})/2$,[1] see section 2.4.2
[c] $E_{int} = 0.429G(\mathbf{r})$,[2] see section 2.4.2
[d] $|E^V_{cont}| = |0.58V(r_{bcp})|$,[3] see section 2.4.3
[e] $|E^G_{cont}| = |-0.57G(r_{bcp})|$,[3] see section 2.4.3

Table 3S. Parameters and calculated energies (kcal/mol) of the Br_3C–Br•••Pt XBs.

Structure	C–Br•••Pt	*d*(Br•••Pt), Å	∠(C–Br•••Pt),°	E_{int}[b]	E_{int}[c]	$\|E^V_{cont}\|$[d]	$\|E^G_{cont}\|$[e]
1•$CHCl_3$•CBr_4	C1S–Br2S•••Pt1	3.6982(8)	161.27(18)	1.3	1.1	1.5	1.8
2•2CBr_4	C1S–Br2S•••Pt1	3.7273(9)	155.33(18)	1.3	1.1	1.5	1.7
	Comparison[a]	*3.6*	*180*				

[a] Comparison with the sum of Bondi vdW radii and with the typical XB's angle.
[b] $E_{int} = -V(\mathbf{r})/2$,[1] see section 2.4.2
[c] $E_{int} = 0.429G(\mathbf{r})$,[2] see section 2.4.2
[d] $|E^V_{cont}| = |0.58V(r_{bcp})|$,[3] see section 2.4.3
[e] $|E^G_{cont}| = |-0.57G(r_{bcp})|$,[3] see section 2.4.3

Table 4S. Parameters and calculated energies (kcal/mol) of the Br_3C–Br•••Br–Br_3C XBs.

Structure	C–Br•••Br–C	*d*(Br•••Br), Å	∠(C–Br•••Br),°	∠(Br•••Br–C),°	E_{int}[b]	E_{int}[c]	$\|E^V_{cont}\|$[d]	$\|E^G_{cont}\|$[e]
2•2CBr_4	C1S–Br2S•••Br4S–C1S	3.7219(11)	110.19(18)	140.9(2)	1.3	1.1	1.2	1.6
3•2CBr_4	C1S–Br4S•••Br8S–C2S	3.4091(13)	169.0(3)	99.9(3)	2.2	1.9		
	C1S–Br3S•••Br8S–C2S	3.6529(14)	134.4(4)	117.3(3)	1.6	1.3		
	Comparison[a]	*3.7*	*90*	*180*				

[a] Comparison with the sum of Bondi vdW radii and with the typical XB's angle.
[b] $E_{int} = -V(\mathbf{r})/2$,[1] see section 2.4.2
[c] $E_{int} = 0.429G(\mathbf{r})$,[2] see section 2.4.2
[d] $|E^V_{cont}| = |0.58V(r_{bcp})|$,[3] see section 2.4.3
[e] $|E^G_{cont}| = |-0.57G(r_{bcp})|$,[3] see section 2.4.3

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Table 5S. Cartesian atomic coordinates of model supramolecular associates.

Atom	X	Y	Z
1•$(CBr_4)_2$•$(CHCl_3)_4$			
Pt	6.940995	5.018738	9.451493
Cl	7.389009	7.188968	8.810681
N	5.377508	5.673150	10.442009
N	3.403542	6.672325	11.523260
C	2.102981	6.434551	10.916474
H	2.217736	5.960994	10.088523
H	1.671153	7.275098	10.746347
H	1.561525	5.911493	11.511918
C	4.464045	6.140468	10.986415
C	3.439686	7.330398	12.833237
H	3.015399	8.189191	12.770857
H	4.352352	7.443029	13.109220
H	2.975147	6.789137	13.475938
Cl	6.492981	2.848508	10.092304
N	8.504481	4.364327	8.460976
N	10.478447	3.365152	7.379725
C	11.779009	3.602926	7.986511
H	11.664254	4.076483	8.814462
H	12.210837	2.762379	8.156638
H	12.320464	4.125984	7.391067
C	9.417944	3.897009	7.916570
C	10.442304	2.707079	6.069748
H	10.866590	1.848286	6.132128
H	9.529638	2.594447	5.793765
H	10.906842	3.248340	5.427047
Br	6.533754	7.390343	3.135816
Br	8.148628	4.669248	3.319364
Br	4.995829	4.645966	3.366433
Br	6.620145	5.814781	5.854065
C	6.578524	5.619599	3.952614
Cl	1.908441	2.382777	11.013824
Cl	3.609179	0.740887	12.709422
Cl	3.466680	3.601459	13.111299
C	3.416164	2.306187	11.922113
H	4.160144	2.431451	11.296424
Cl	3.975248	7.654700	7.889161
Cl	2.274510	9.296589	6.193563
Cl	2.417009	6.436018	5.791686
C	2.467525	7.731290	6.980872
H	1.723546	7.606026	7.606561
Cl	9.906741	2.382777	11.013824
Cl	11.607479	0.740887	12.709422
Cl	11.464980	3.601459	13.111299
C	11.414464	2.306187	11.922113
H	12.158444	2.431451	11.296424
Br	7.348235	2.647134	15.767169

Br	5.733361	5.368229	15.583621
Br	8.886161	5.391511	15.536552
Br	7.261844	4.222696	13.048920
C	7.303465	4.417878	14.950371
Cl	11.973548	7.654700	7.889161
Cl	10.272810	9.296589	6.193563
Cl	10.415309	6.436018	5.791686
C	10.465825	7.731290	6.980872
H	9.721846	7.606026	7.606561
1•$(CBr_4)_6$			
Pt	5.443549	10.824233	0.000000
Cl	6.238769	10.291304	2.086133
N	5.239594	8.910846	-0.432878
N	5.117235	6.590224	-1.171985
C	5.203482	7.821625	-0.763681
C	5.724531	5.503497	-0.383731
H	6.457075	5.123456	-0.875208
H	5.066473	4.824310	-0.215494
H	6.044727	5.853782	0.449891
C	4.613268	6.281510	-2.510316
H	4.285652	7.084783	-2.920511
H	3.901830	5.641931	-2.444156
H	5.323971	5.917193	-3.041490
Cl	4.648328	11.357162	-2.086133
N	5.647504	12.737620	0.432878
N	5.769862	15.058242	1.171985
C	5.683616	13.826841	0.763681
C	5.162567	16.144970	0.383731
H	4.430022	16.525011	0.875208
H	5.820625	16.824157	0.215494
H	4.842370	15.794684	-0.449891
C	6.273829	15.366956	2.510316
H	6.601445	14.563683	2.920511
H	6.985267	16.006535	2.444156
H	5.563127	15.731273	3.041490
Br	6.533754	7.390343	3.135816
Br	8.148628	4.669248	3.319364
Br	4.995829	4.645966	3.366433
Br	6.620145	5.814781	5.854065
C	6.578524	5.619599	3.952614
Br	10.162786	14.606498	3.135816
Br	11.777661	11.885404	3.319364
Br	8.624861	11.862121	3.366433
Br	10.249178	13.030936	5.854065
C	10.207556	12.835754	3.952614
Br	2.164486	14.606498	3.135816
Br	3.779361	11.885404	3.319364
Br	0.626561	11.862121	3.366433
Br	2.250878	13.030936	5.854065
C	2.209256	12.835754	3.952614

Br	4.353343	14.258124	-3.135816
Br	2.738469	16.979218	-3.319364
Br	5.891269	17.002501	-3.366433
Br	4.266952	15.833685	-5.854065
C	4.308573	16.028868	-3.952614
Br	0.724311	7.041968	-3.135816
Br	-0.890564	9.763062	-3.319364
Br	2.262236	9.786345	-3.366433
Br	0.637920	8.617530	-5.854065
C	0.679541	8.812712	-3.952614
Br	8.722611	7.041968	-3.135816
Br	7.107736	9.763062	-3.319364
Br	10.260536	9.786345	-3.366433
Br	8.636220	8.617530	-5.854065
C	8.677841	8.812712	-3.952614
2•$(CBr_4)_8$			
Pt	7.716447	9.244155	5.649941
Cl	7.865496	8.119618	7.653975
N	9.531123	8.704951	5.180996
N	11.603665	7.928526	4.131237
C	10.505228	8.321318	4.684931
C	12.221363	8.761100	3.084868
H	13.185438	8.739139	3.192217
H	11.930980	9.679656	3.198996
C	11.872544	8.307231	1.711932
H	12.302709	8.883484	1.071229
H	10.924646	8.349469	1.592153
H	12.177962	7.408458	1.586503
C	12.168155	6.620478	4.405824
H	12.154121	6.099661	3.587712
H	13.096204	6.732516	4.665721
C	11.485758	5.872017	5.442023
H	11.253852	6.464238	6.162955
H	12.059795	5.178839	5.769720
H	10.684582	5.483459	5.080427
Cl	7.567398	10.368693	3.645907
N	5.901771	9.783360	6.118886
N	3.829229	10.559784	7.168645
C	4.927666	10.166993	6.614951
C	3.211531	9.727211	8.215014
H	2.247456	9.749172	8.107665
H	3.501914	8.808655	8.100885
C	3.560350	10.181079	9.587950
H	3.130185	9.604827	10.228653
H	4.508248	10.138842	9.707728
H	3.254932	11.079853	9.713378
C	3.264738	11.867833	6.894058
H	3.278773	12.388650	7.712169
H	2.336689	11.755794	6.634161
C	3.947136	12.616294	5.857859

H	4.179042	12.024073	5.136926
H	3.373099	13.309472	5.530162
H	4.748312	13.004852	6.219455
Br	3.994685	3.614076	8.670399
Br	5.410567	6.407338	9.029509
Br	2.280712	6.186359	9.297769
Br	4.130236	4.948465	11.530964
C	3.956736	5.298673	9.624109
Br	8.053687	9.931684	13.929364
Br	6.637805	7.138423	13.570254
Br	9.767660	7.359401	13.301995
Br	7.918136	8.597295	11.068799
C	8.091636	8.247087	12.975654
Br	12.026685	3.614076	8.670399
Br	13.442567	6.407338	9.029509
Br	10.312712	6.186359	9.297769
Br	12.162236	4.948465	11.530964
C	11.988736	5.298673	9.624109
Br	3.406209	14.874234	2.629482
Br	1.990327	12.080973	2.270372
Br	5.120182	12.301951	2.002113
Br	3.270658	13.539845	-0.231083
C	3.444158	13.189637	1.675772
Br	7.379207	8.556627	-2.629482
Br	8.795089	11.349888	-2.270372
Br	5.665234	11.128910	-2.002113
Br	7.514758	9.891015	0.231083
C	7.341258	10.241224	-1.675772
Br	11.438209	14.874234	2.629482
Br	10.022327	12.080973	2.270372
Br	13.152182	12.301951	2.002113
Br	11.302658	13.539845	-0.231083
C	11.476158	13.189637	1.675772
Br	7.843070	7.063947	2.629482
Br	6.427188	4.270686	2.270372
Br	9.557043	4.491664	2.002113
Br	7.707520	5.729558	-0.231083
C	7.881020	5.379350	1.675772
Br	7.589824	11.424363	8.670399
Br	9.005706	14.217625	9.029509
Br	5.875851	13.996646	9.297769
Br	7.725374	12.758752	11.530964
C	7.551874	13.108960	9.624109
3•$(CBr_4)_7$			
Pt	2.977887	8.071811	2.479022
Cl	3.320895	6.256326	3.868274
Cl	2.634775	9.908685	1.121549
N	1.338649	7.230180	1.800796
N	4.630130	8.884598	3.141637
N	-0.704196	6.227159	0.907832

C	0.384224	6.748924	1.386372
C	8.268327	10.890641	5.465575
H	8.477660	11.778615	5.794513
H	8.598649	10.232763	6.097434
C	-2.748867	5.070200	0.800973
H	-2.528554	4.138476	0.951504
H	-3.700157	5.198211	0.943142
C	5.603779	9.294557	3.597876
C	-1.922755	5.992202	1.729248
H	-2.391050	6.821842	1.914159
H	-1.707116	5.553077	2.566460
C	6.752997	10.726982	5.239779
H	6.315984	10.372116	6.028673
H	6.339568	11.571205	4.999115
C	8.043715	9.535995	3.498451
H	8.004837	9.604052	2.532080
H	8.405041	8.670707	3.744690
C	-2.342605	5.507706	-0.597478
H	-2.802465	6.322762	-0.853009
H	-2.540795	4.815799	-1.247920
C	-0.842283	5.739421	-0.487832
H	-0.346700	4.917884	-0.625354
H	-0.540319	6.405402	-1.125266
C	8.856310	10.670268	4.102434
H	9.792357	10.423969	4.168407
H	8.781101	11.472361	3.562566
N	6.703094	9.764470	4.115443
Br	5.978111	6.209172	5.501350
Br	7.561256	4.377322	7.569943
Br	9.140820	6.070953	5.421531
Br	7.661589	7.514559	7.828633
C	7.588658	6.040814	6.549027
Br	-1.683890	8.714133	-2.938327
Br	-0.017810	9.951301	-0.535779
Br	-3.173559	9.834795	-0.380137
Br	-1.806244	11.817990	-2.394093
C	-1.641053	10.078826	-1.564779
Br	6.911410	8.714133	-2.938327
Br	8.577490	9.951301	-0.535779
Br	5.421741	9.834795	-0.380137
Br	6.789056	11.817990	-2.394093
C	6.954247	10.078826	-1.564779
Br	1.133076	6.209172	-3.790686
Br	2.716221	4.377322	-1.722093
Br	4.295785	6.070953	-3.870504
Br	2.816554	7.514559	-1.463403
C	2.743623	6.040814	-2.743009
Br	3.161145	8.714133	6.353708
Br	4.827225	9.951301	8.756257
Br	1.671476	9.834795	8.911898

Br	3.038791	11.817990	6.897943
C	3.203982	10.078826	7.727257
Br	-2.617189	6.209172	5.501350
Br	-1.034044	4.377322	7.569943
Br	0.545520	6.070953	5.421531
Br	-0.933711	7.514559	7.828633
C	-1.006642	6.040814	6.549027
Br	1.683890	0.612183	2.938327
Br	0.017810	1.849351	0.535779
Br	3.173559	1.732845	0.380137
Br	1.806244	3.716040	2.394093
C	1.641053	1.976876	1.564779