Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

The first bismuth-NHC complexes

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Cartesian coordinates of optimized geometries.

NHC^{Me}-$BiCl_3$

M06-2X/def2-SV(P)

Bi	0.921566	0.163873	-0.327580
Cl	1.609656	-1.058949	1.731166
Cl	0.702944	2.499540	0.885336
Cl	0.287996	-1.985884	-1.723364
C	-1.389364	0.000377	0.128205
N	-2.048378	-1.003667	0.732577
N	-2.329266	0.878717	-0.269584
C	-3.580970	0.432664	0.088696
C	-3.401385	-0.754740	0.725581
C	-1.449209	-2.215246	1.290160
C	-2.084543	2.093892	-1.039658
H	-4.482973	0.993435	-0.141510
H	-4.115745	-1.442038	1.171092
H	-2.971728	2.736990	-0.963148
H	-2.253527	-2.949049	1.435068
H	-1.215730	2.617467	-0.611756
H	-0.714619	-2.604417	0.570084
H	-0.955721	-1.990204	2.245082
H	-1.913754	1.839275	-2.097944

M06-2X/def2-TZVP

Bi	0.905430	0.180834	-0.330317
Cl	1.666157	-1.017261	1.674044
Cl	0.628772	2.466239	0.952483
Cl	0.327000	-1.984149	-1.718645
C	-1.371849	-0.027953	0.127750
N	-2.026061	-1.000958	0.777706
N	-2.314881	0.820260	-0.313594
C	-3.562136	0.385969	0.064152
C	-3.378254	-0.759433	0.756565
C	-1.424563	-2.178264	1.399417
C	-2.074199	1.985397	-1.156645
H	-4.456949	0.923666	-0.192317
H	-4.081685	-1.419799	1.230699
H	-2.986898	2.573839	-1.195468
H	-2.214262	-2.907322	1.560753
H	-1.276281	2.584881	-0.722662
H	-0.677752	-2.591441	0.725282
H	-0.962226	-1.907181	2.344832
H	-1.814800	1.662628	-2.165029

NHC^{Ph}-$BiCl_3$

M06-2X/def2-SV(P)

Bi	0.234774	-1.249074	-0.186198
Cl	-2.105116	-1.580279	-0.980299
Cl	-0.232117	-1.267627	2.451808
Cl	1.178797	-0.237745	-2.415635
C	0.008031	1.059625	0.215916
N	-1.048941	1.886342	0.229417
N	1.094639	1.849690	0.298422
C	0.726651	3.181443	0.334930
C	-0.630403	3.204084	0.292458
H	1.461083	3.977888	0.421314
H	-1.341895	4.024764	0.330244
C	-2.427548	1.481769	0.211493
C	-3.222168	1.843410	-0.873135
C	-2.922734	0.724857	1.268928
C	-4.551923	1.431604	-0.898675
H	-2.789458	2.412335	-1.699665
C	-4.252885	0.312794	1.225916
H	-2.258332	0.423411	2.083706
C	-5.064773	0.664568	0.148165
H	-5.183620	1.695581	-1.749659
H	-4.650703	-0.299575	2.037914
H	-6.104770	0.331112	0.117937
C	2.438090	1.357602	0.336608
C	2.786040	0.432600	1.321010
C	3.352127	1.782235	-0.625358
C	4.084528	-0.081194	1.329646
H	2.044988	0.115713	2.064063
C	4.648246	1.276998	-0.591108
H	3.028506	2.462649	-1.415588
C	5.014115	0.344757	0.382386
H	4.368297	-0.808716	2.093442
H	5.370659	1.594942	-1.345941
H	6.030172	-0.056071	0.396870

M06-2X/def2-TZVP

Bi	0.254237	-1.236463	-0.213220
Cl	-2.037487	-1.609674	-1.014249
Cl	-0.267232	-1.465579	2.384921
Cl	1.096264	-0.131922	-2.445507
C	0.003520	1.036939	0.274496
N	-1.052165	1.862020	0.287137
N	1.084070	1.831592	0.365996
C	0.711548	3.158716	0.405922
C	-0.636549	3.177497	0.358325
H	1.435128	3.948460	0.497971
H	-1.342378	3.987454	0.397115
C	-2.432830	1.470757	0.252062
C	-3.213499	1.876959	-0.817524
C	-2.941830	0.701709	1.283725
C	-4.545202	1.495782	-0.854353
H	-2.770465	2.451315	-1.621311
C	-4.274016	0.320813	1.229838
H	-2.294866	0.380623	2.090722
C	-5.073211	0.716929	0.166948
H	-5.164175	1.791539	-1.690717
H	-4.682228	-0.296133	2.018870
H	-6.110357	0.410523	0.128675
C	2.431810	1.355355	0.386415
C	2.794246	0.402539	1.327084
C	3.332660	1.834362	-0.552016
C	4.093726	-0.090003	1.311518
H	2.073105	0.062356	2.063550
C	4.629047	1.348657	-0.542664
H	3.000248	2.537093	-1.304719
C	5.008665	0.384712	0.383572
H	4.388098	-0.836196	2.037536
H	5.338078	1.705295	-1.277622
H	6.020004	0.000500	0.377416

NHC^{dipp}-$BiCl_3$

M06-2X/def2-SV(P)

Bi	0.18711700	-0.00030400	-1.73150100	H	-3.59049800	3.31351700	2.69563200
Cl	-2.25889100	-0.00009500	-2.18735000	H	-2.63945900	3.12296600	-0.97759800
Cl	0.20787800	-2.62387300	-1.41797500	H	-3.74636300	3.94130200	0.18208800
Cl	0.20855600	2.62335600	-1.41891900	H	-2.03719700	4.43798400	0.05671800
C	0.03912800	0.00003600	0.62322700	C	-2.31282500	-2.55758700	1.09750300
N	-1.00525900	-0.00000100	1.46599400	C	-2.71919200	-3.57069100	0.02531300
N	1.14473900	-0.00000100	1.39597700	C	-2.52102200	-3.12436700	2.50791500
C	0.79432900	-0.00012200	2.73163400	H	-1.23571000	-2.37322600	0.95425000
C	-0.56414900	-0.00011400	2.77396700	H	-2.64009400	-3.12202700	-0.97746400
H	1.53708700	-0.00017600	3.52374200	H	-2.03898500	-4.43746800	0.05696100
H	-1.26222500	-0.00011700	3.60686800	H	-3.74794800	-3.93987900	0.18167700
C	-2.40527800	0.00029400	1.10639700	H	-2.15994000	-2.42820000	3.28446800
C	-3.04507200	1.23737400	0.94152300	H	-3.59271400	-3.31270600	2.69530100
C	-3.04569500	-1.23648900	0.94171300	H	-1.97894700	-4.07837500	2.62334400
C	-4.40602700	1.20847700	0.62698400	C	2.50246500	-2.55422700	1.07710400
C	-4.40663900	-1.20694600	0.62718500	C	2.90750700	-2.80929000	2.53770900
C	-5.08004900	0.00092300	0.47503500	C	2.90437200	-3.75047100	0.21269700
H	-4.94251300	2.14849600	0.48206700	H	1.40584800	-2.46505100	1.02264900
H	-4.94361200	-2.14671400	0.48243000	H	2.58393700	-1.99892700	3.21057700
H	-6.14285600	0.00116100	0.22068000	H	2.45805900	-3.75015500	2.89788900
C	2.48839800	-0.00003800	0.86255400	H	4.00464200	-2.89794600	2.62162100
C	3.10517900	-1.24064700	0.60644000	H	2.72953000	-3.54813400	-0.85430700
C	3.10517600	1.24054500	0.60630300	H	3.96264800	-4.02313400	0.36984000
C	4.36027500	-1.20859700	-0.00963100	H	2.29168000	-4.62394900	0.48922000
C	4.36028400	1.20843400	-0.00974500	C	2.50240500	2.55419300	1.07675100
C	4.97204400	-0.00009800	-0.32897600	C	2.90454700	3.75035600	0.21234200
H	4.86646100	-2.14676200	-0.24355300	C	2.90708800	2.80935700	2.53742500
H	4.86646800	2.14657300	-0.24376300	H	1.40580500	2.46502500	1.02200300
H	5.94770500	-0.00013700	-0.82120800	H	2.72998100	3.54790800	-0.85468600
C	-2.31157500	2.55814300	1.09717100	H	2.29178300	4.62386000	0.48862800
C	-2.51895600	3.12484000	2.50774100	H	3.96277900	4.02303200	0.36974700
C	-2.71787200	3.57156900	0.02526200	H	2.58313300	1.99917800	3.21032600
H	-1.23459500	2.37333700	0.95347600	H	4.00422000	2.89777800	2.62163800
H	-2.15773700	2.42846700	3.28404100	H	2.45776400	3.75037800	2.89735700
H	-1.97650500	4.07865400	2.62302300				

NHC^{dipp}-$BiCl_3$

M06-2X/def2-TZVP

Bi	1.74202896	-0.18890988	0.00000000
Cl	2.21949990	2.21653713	0.00000000
Cl	1.48179688	-0.19079890	-2.62197706
Cl	1.48179688	-0.19079890	2.62197706
C	-0.60330604	-0.03949794	-0.00000000
N	-1.44695507	1.00195203	-0.00000000
N	-1.37927201	-1.14064596	-0.00000000
C	-2.71124102	-0.78819800	-0.00000000
C	-2.75229306	0.56139000	-0.00000000
H	-3.49535600	-1.52235202	-0.00000000
H	-3.57631108	1.25195098	-0.00000000
C	-1.10093711	2.40477204	-0.00000000
C	-0.95137208	3.04391705	1.23146801
C	-0.95137208	3.04391705	-1.23146801
C	-0.65435312	4.40219906	1.20217700
C	-0.65435312	4.40219906	-1.20217700
C	-0.50989918	5.07418606	-0.00000000
H	-0.51955110	4.93513207	2.13371199
H	-0.51955110	4.93513207	-2.13371199
H	-0.26961921	6.12982907	-0.00000000
C	-0.86874598	-2.49237695	-0.00000000
C	-0.63395900	-3.11382195	-1.23442198
C	-0.63395900	-3.11382195	1.23442198
C	-0.05974897	-4.38121693	-1.20205200
C	-0.05974897	-4.38121693	1.20205200
C	0.23851609	-4.99929292	-0.00000000
H	0.15708202	-4.88843293	-2.13192200
H	0.15708202	-4.88843293	2.13192200
H	0.69534512	-5.98087091	-0.00000000
C	-1.11361102	2.31648905	2.55037002
C	-2.53048901	2.51669302	3.09741606
C	-0.07085000	2.74920608	3.57975198
H	-0.95922000	1.24957605	2.37770002
H	-3.28804002	2.14377699	2.40570509
H	-2.64781996	1.99162102	4.04694407
H	-2.72489803	3.57785201	3.26839107
H	0.93257799	2.71115311	3.15606495
H	-0.26658301	3.75874208	3.94726199
H	-0.09707295	2.07168208	4.43364799
C	-1.11361102	2.31648905	-2.55037002
C	-0.07085000	2.74920608	-3.57975198
C	-2.53048901	2.51669302	-3.09741606
H	-0.95922000	1.24957605	-2.37770002
H	0.93257799	2.71115311	-3.15606495
H	-0.09707295	2.07168208	-4.43364799
H	-0.26658301	3.75874208	-3.94726199
H	-3.28804002	2.14377699	-2.40570509
H	-2.72489803	3.57785201	-3.26839107
H	-2.64781996	1.99162102	-4.04694407
C	-1.07715206	-2.49768096	-2.54685197
C	-2.53863306	-2.87829700	-2.82022592
C	-0.21424409	-2.91854095	-3.73443800
H	-1.00773509	-1.41193496	-2.45781897
H	-3.20950904	-2.54537602	-2.02876590
H	-2.87307110	-2.43081902	-3.75762591
H	-2.63516803	-3.96286501	-2.90670391
H	0.84593791	-2.78895892	-3.52568903
H	-0.40431707	-3.95766195	-4.01207899
H	-0.46069413	-2.29876895	-4.59686399
C	-1.07715206	-2.49768096	2.54685197
C	-0.21424409	-2.91854095	3.73443800
C	-2.53863306	-2.87829700	2.82022592
H	-1.00773509	-1.41193496	2.45781897
H	0.84593791	-2.78895892	3.52568903
H	-0.46069413	-2.29876895	4.59686399
H	-0.40431707	-3.95766195	4.01207899
H	-3.20950904	-2.54537602	2.02876590
H	-2.63516803	-3.96286501	2.90670391
H	-2.87307110	-2.43081902	3.75762591

Table S1. Crystal data and structure refinement for compound **9**.

Identification code	**9**	
Empirical formula	$C_{31}H_{46}Bi_1Cl_3N_2O_1$	
Formula weight	778.03	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.334(3) Å	α= 90°.
	b = 15.235(3) Å	β= 103.87(3)°.
	c = 19.277(4) Å	γ = 90°.
Volume	3516.9(12) $Å^3$	
Z	4	
Density (calculated)	1.469 Mg/m^3	
Absorption coefficient	5.265 mm^{-1}	
F(000)	1552	
Crystal size	0.25 x 0.12 x 0.07 mm^3	
Theta range for data collection	3.22 to 24.71°.	
Index ranges	-12<=h<=14, -17<=k<=17, -22<=l<=22	
Reflections collected	27630	
Independent reflections	5972 [R(int) = 0.1238]	
Completeness to theta = 24.71°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7095 and 0.3528	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5972 / 6 / 343	
Goodness-of-fit on F^2	0.814	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.0690	
R indices (all data)	R1 = 0.1140, wR2 = 0.0796	
Largest diff. peak and hole	2.671 and -0.782 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for compound **11**.

Identification code	**11**	
Empirical formula	$C_{16}H_{28}Bi_1Cl_2F_3N_2O_4S_1$	
Formula weight	681.34	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.415(2) Å	α= 102.25(3) °
	b = 10.538(2) Å	β= 92.74(3) °
	c = 12.433(3) Å	γ = 95.89(3) °.
Volume	1195.1(4) $Å^3$	
Z	2	
Density (calculated)	1.892 Mg/m^3	
Absorption coefficient	7.728 mm^{-1}	
F(000)	660	
Crystal size	0.25 x 0.18 x 0.15 mm^3	
Theta range for data collection	2.87 to 25.03°.	
Index ranges	-10<=h<=11, -12<=k<=12, -14<=l<=14	
Reflections collected	9400	
Independent reflections	4231 [R(int) = 0.0761]	
Completeness to theta = 24.71°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3902 and 0.2482	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4231 / 0 / 262	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0556, wR2 = 0.1202	
R indices (all data)	R1 = 0.0733, wR2 = 0.1303	
Largest diff. peak and hole	2.892 and -2.147 $e.Å^{-3}$	