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Supporting Information

Dynamic Behaviour Attributed to Chiral Carbohydrate Substituents of N-Heterocyclic Carbene Ligands in a Square Planar Nickel Complex

Teppei Shibata, Satoru Ito, Matsumi Doe, Rika Tanaka, Hideki Hashimoto, Isamu Kinoshita, Shigenobu Yano and Takanori Nishioka,*

DFT Calculations: DFT calculations were carried out for two diastereomers of each of *syn*- and *anti*-isomers using Gaussian03W.[s1] Atomic coordinates were optimized at B3LYP/6-311G(d) level. Calculations of NMR chemical shifts were carried out by using optimized structures. Structural optimization for the virtual molecule of *anti*-*R*-[$NiBr_2(magi)_2$] gave another *anti*-*S*-[$NiBr_2(magi)_2$] with the smaller tilt angle of the imizadolylidene rings.

Table S1. Optimized atomic coordinates of *syn*-*R*-[$NiBr_2(magi)_2$]

number	atoms	*x*	*y*	*z*
1	Br	3.148071	-1.236103	-1.836958
2	Br	0.721915	-3.695655	1.384585
3	Ni	1.881897	-2.364859	-0.180493
4	O	3.439307	1.578109	0.943936
5	O	0.668845	0.107407	2.799201
6	O	1.692604	-0.006768	4.818039
7	O	-0.017123	2.905294	2.691799
8	8	-1.872561	1.748577	2.093534
9	O	0.927200	4.134294	0.240186
10	O	1.265956	5.947458	1.557462
11	O	4.838896	3.013744	-1.073512
12	O	3.520274	3.473106	-2.847078
13	O	-2.523404	-2.012502	-0.387871
14	O	-0.597928	0.565031	-2.115589
15	O	-1.027878	0.271554	-4.323167
16	O	-3.279221	1.682089	-1.969805
17	O	-2.402827	3.505574	-0.946892
18	O	-4.663638	0.834294	0.442324
19	O	-6.450453	0.660779	-0.942939
20	O	-5.346659	-2.452502	0.258104
21	O	-6.981825	-1.625041	1.588299
22	N	3.301819	-0.599625	1.714667
23	N	4.115362	-2.580473	1.771597
24	N	-0.689334	-2.393178	-1.711917
25	N	0.726654	-3.836399	-2.426293
26	C	3.164991	-1.838579	1.161019

27	C	4.327055	-0.571835	2.651927
28	C	4.839379	-1.820180	2.683293
29	C	4.378705	-3.984790	1.475661
30	C	2.535772	0.547478	1.287975
31	C	1.585121	1.108007	2.355973
32	C	0.789672	2.241532	1.705961
33	C	1.718349	3.290448	1.088215
34	C	2.800511	2.627292	0.215004
35	C	3.879542	3.617042	-0.192780
36	C	0.821283	-0.373707	4.075480
37	C	-0.238798	-1.392457	4.375313
38	C	-1.335725	2.582355	2.775548
39	C	-2.004459	3.416338	3.836006
40	C	0.751110	5.443657	0.595461
41	C	-0.147746	6.124599	-0.399444
42	C	4.521306	2.977661	-2.390871
43	C	5.563090	2.221183	-3.169103
44	C	0.573083	-2.863071	-1.500233
45	C	-1.313931	-3.083294	-2.747160
46	C	-0.420462	-3.988653	-3.194337
47	C	1.930436	-4.648012	-2.567611
48	C	-1.366933	-1.389278	-0.912025
49	C	-1.774812	-0.166200	-1.759056
50	C	-2.726835	0.766113	-1.003377
51	C	-3.872676	-0.031067	-0.387374
52	C	-3.289732	-1.161799	0.471187
53	C	-4.328345	-2.012533	1.177050
54	C	-0.329985	0.726124	-3.456962
55	C	0.928340	1.517650	-3.646574
56	C	-3.046676	3.012519	-1.837455
57	C	-3.705795	3.757855	-2.969657
58	C	-5.950558	1.081952	0.068381
59	C	-6.653154	1.906223	1.111611
60	C	-6.639944	-2.181069	0.574330
61	C	-7.564920	-2.626913	-0.524820
62	H	4.589696	0.317681	3.196020
63	H	5.642323	-2.236275	3.268100
64	H	3.446349	-4.544514	1.521828
65	H	5.072427	-4.376887	2.218371
66	H	4.822711	-4.083283	0.483781
67	H	1.973546	0.220343	0.408598
68	H	2.157673	1.474507	3.209166

69	H	0.134601	1.834741	0.934110
70	H	2.167751	3.895547	1.878105
71	H	2.326738	2.209500	-0.680858
72	H	3.427486	4.483029	-0.674804
73	H	4.451604	3.928857	0.681083
74	H	-1.229712	-0.967464	4.200412
75	H	-0.146968	-1.719485	5.408967
76	H	-0.121801	-2.242492	3.697896
77	H	-1.501413	3.280509	4.795841
78	H	-3.050902	3.131277	3.919433
79	H	-1.926356	4.475037	3.578726
80	H	0.365237	6.196334	-1.362642
81	H	-0.390511	7.124477	-0.044923
82	H	-1.051057	5.532752	-0.557551
83	H	6.568056	2.476721	-2.831036
84	H	5.450858	2.430194	-4.231268
85	H	5.417058	1.150823	-2.997128
86	H	-2.324879	-2.878992	-3.051048
87	H	-0.492980	-4.719783	-3.981716
88	H	2.792351	-4.000472	-2.721754
89	H	1.811705	-5.305041	-3.428298
90	H	2.078090	-5.254197	-1.672911
91	H	-0.681381	-1.099717	-0.109533
92	H	-2.266447	-0.500535	-2.673410
93	H	-2.208229	1.333242	-0.230691
94	H	-4.506256	-0.447214	-1.169860
95	H	-2.636390	-0.733847	1.243840
96	H	-3.841444	-2.903401	1.575864
97	H	-4.792571	-1.452946	1.986796
98	H	0.908654	2.440839	-3.066220
99	H	1.062003	1.744236	-4.702134
100	H	1.776120	0.928049	-3.289228
101	H	-3.237401	3.476088	-3.915971
102	H	-3.605140	4.830308	-2.815980
103	H	-4.760122	3.483340	-3.038863
104	H	-7.064340	1.219745	1.857318
105	H	-7.476864	2.451302	0.653154
106	H	-5.966549	2.588418	1.611974
107	H	-7.664985	-1.798751	-1.232049
108	H	-8.547292	-2.845919	-0.108837
109	H	-7.169238	-3.490852	-1.057769

Table S2. Optimized atomic coordinates of *syn-S*-[$NiBr_2(magi)_2$]

number	atoms	*x*	*y*	*z*
1	Br	0.136348	-3.458828	-1.563674
2	Br	2.135313	-1.817380	2.383147
3	Ni	1.136179	-2.606593	0.398197
4	O	2.450090	0.536766	-2.054131
5	O	4.381515	0.753200	1.038668
6	O	6.463974	0.214492	0.329047
7	O	4.369900	3.441008	0.053625
8	O	3.349675	4.229227	1.921491
9	O	1.838477	4.056684	-1.210980
10	O	2.583252	5.098076	-3.079002
11	O	0.339070	0.901311	-3.853753
12	O	-1.204284	1.072701	-2.228632
13	O	-1.953009	0.005522	1.707663
14	O	-3.364377	-2.102245	-0.925981
15	O	-4.756352	-3.504759	0.183706
16	O	-5.220373	0.122834	-0.767989
17	O	-4.833315	0.173648	-3.003766
18	O	-3.883288	2.584363	-0.028593
19	O	-5.746360	2.923669	1.219286
20	O	-2.872112	2.381262	3.181528
21	O	-3.233482	4.593510	2.857811
22	N	3.448284	-1.242207	-0.963482
23	N	3.628392	-3.378483	-0.931082
24	N	-1.657296	-2.271709	1.505933
25	N	-0.617421	-3.990764	2.257273
26	C	2.809760	-2.375154	-0.541671
27	C	4.627558	-1.550072	-1.636548
28	C	4.741090	-2.892826	-1.606718
29	C	3.377426	-4.792949	-0.677081
30	C	2.919881	0.090558	-0.792270
31	C	3.958645	1.105471	-0.277438
32	C	3.319382	2.492209	-0.194117
33	C	2.612985	2.876010	-1.492677
34	C	1.686988	1.737248	-1.949880
35	C	1.063140	2.017462	-3.311672
36	C	5.655560	0.297359	1.216678
37	C	5.864906	-0.083167	2.655013
38	C	4.271419	4.247285	1.153011
39	C	5.480003	5.143044	1.239360
40	C	1.938375	5.116401	-2.064456

41	C	1.122708	6.272702	-1.550264
42	C	-0.798252	0.527491	-3.234400
43	C	-1.458376	-0.633523	-3.916040
44	C	-0.478841	-2.953331	1.399827
45	C	-2.489415	-2.858011	2.456771
46	C	-1.836202	-3.941100	2.920703
47	C	0.399098	-5.010747	2.485298
48	C	-1.990689	-1.062874	0.778022
49	C	-3.392179	-1.143778	0.135380
50	C	-3.818349	0.206428	-0.444903
51	C	-3.636857	1.310418	0.591740
52	C	-2.192230	1.285198	1.111178
53	C	-1.878070	2.355515	2.139671
54	C	-4.072761	-3.260128	-0.775825
55	C	-3.854991	-4.153456	-1.964232
56	C	-5.595492	0.119290	-2.074511
57	C	-7.097187	0.030041	-2.174473
58	C	-4.957373	3.309138	0.396019
59	C	-4.979642	4.658762	-0.267299
60	C	-3.488259	3.565249	3.434335
61	C	-4.548207	3.401992	4.489119
62	H	5.282778	-0.801174	-2.042295
63	H	5.508855	-3.541955	-1.992553
64	H	3.291577	-4.966677	0.395750
65	H	4.215886	-5.371823	-1.062322
66	H	2.458858	-5.099772	-1.175054
67	H	2.100393	0.007402	-0.072349
68	H	4.823483	1.139373	-0.940811
69	H	2.615460	2.528263	0.639161
70	H	3.344109	3.106772	-2.268943
71	H	0.892384	1.602128	-1.209820
72	H	0.397393	2.878270	-3.232317
73	H	1.835343	2.222721	-4.051484
74	H	5.624237	0.757145	3.309526
75	H	6.896219	-0.395490	2.805664
76	H	5.178721	-0.894083	2.912495
77	H	6.389152	4.541377	1.306676
78	H	5.395341	5.785493	2.113168
79	H	5.563491	5.751579	0.336097
80	H	0.066282	5.995801	-1.513188
81	H	1.253542	7.131553	-2.204959
82	H	1.422891	6.523821	-0.530979

83	H	-1.130128	-0.727861	-4.950071
84	H	-2.540264	-0.517667	-3.855431
85	H	-1.179750	-1.544063	-3.376144
86	H	-3.460548	-2.469707	2.702525
87	H	-2.127340	-4.680410	3.647523
88	H	0.676580	-5.471760	1.537499
89	H	-0.013047	-5.776017	3.142007
90	H	1.277481	-4.562131	2.948325
91	H	-1.235611	-0.940151	-0.003474
92	H	-4.131650	-1.455855	0.872967
93	H	-3.249932	0.439847	-1.344290
94	H	-4.333878	1.177672	1.418160
95	H	-1.508224	1.430104	0.264497
96	H	-0.920552	2.125315	2.608906
97	H	-1.828267	3.334630	1.667519
98	H	-4.089569	-3.620923	-2.888184
99	H	-4.476822	-5.041657	-1.872554
100	H	-2.799333	-4.433061	-2.010308
101	H	-7.437051	-0.928172	-1.773542
102	H	-7.400593	0.119635	-3.215460
103	H	-7.564589	0.813179	-1.574439
104	H	-4.377416	5.337187	0.343960
105	H	-6.000960	5.035663	-0.294566
106	H	-4.552818	4.623278	-1.269168
107	H	-5.479127	3.124702	3.986563
108	H	-4.702014	4.350425	5.001770
109	H	-4.291124	2.616024	5.198489

Table S3. Optimized atomic coordinates of *anti-S*-[$NiBr_2(magi)_2$]

number	atoms	*x*	*y*	*z*
1	Br	0.150842	1.318387	-0.244028
2	Br	0.418619	-3.385551	0.253583
3	Ni	0.289565	-1.031329	0.010493
4	O	3.715768	1.129398	-1.694542
5	O	4.319516	-2.026254	0.029768
6	O	5.074399	-3.326787	-1.666390
7	O	6.779682	-0.567571	0.377861
8	O	6.469654	-0.882618	2.603890
9	O	6.245682	2.247656	0.712508
10	O	7.780686	3.185562	-0.661584
11	O	3.242133	3.985072	-1.784063
12	O	3.391332	4.974533	0.240665
13	O	-3.345113	1.055517	1.242321
14	O	-3.604049	-2.438081	0.213595
15	O	-4.257444	-3.437369	2.140472
16	O	-6.199486	-1.357125	-0.410144
17	O	-5.869245	-1.998599	-2.561350
18	O	-6.035612	1.444480	-1.195829
19	O	-7.979202	1.576424	-0.035756
20	O	-5.303790	3.244650	1.594518
21	O	-6.543316	4.656383	0.329203
22	N	2.489832	-0.802875	-1.965279
23	N	0.745989	-1.697110	-2.835670
24	N	-1.951550	-0.649604	1.912203
25	N	-0.132689	-1.131515	2.940401
26	C	1.207183	-1.171297	-1.679097
27	C	2.814553	-1.092668	-3.285853
28	C	1.717030	-1.656852	-3.830103
29	C	-0.584198	-2.258450	-3.039210
30	C	3.351462	-0.078272	-1.056656
31	C	4.639289	-0.832801	-0.690280
32	C	5.490682	0.049412	0.223673
33	C	5.697318	1.450246	-0.351431
34	C	4.355992	2.050752	-0.809061
35	C	4.515496	3.358860	-1.568976
36	C	4.594330	-3.230340	-0.568995
37	C	4.200325	-4.358467	0.339222
38	C	7.151747	-0.991018	1.621248
39	C	8.526423	-1.605134	1.562218
40	C	7.288192	3.079218	0.430611

41	C	7.689041	3.842066	1.664381
42	C	2.771916	4.756431	-0.770724
43	C	1.388293	5.257485	-1.083071
44	C	-0.630064	-0.919640	1.701830
45	C	-2.263958	-0.683135	3.266628
46	C	-1.118194	-0.986231	3.910752
47	C	1.264000	-1.416309	3.249309
48	C	-2.865287	-0.224646	0.876092
49	C	-4.064063	-1.165598	0.676246
50	C	-4.992072	-0.580621	-0.390819
51	C	-5.347227	0.870983	-0.071432
52	C	-4.069285	1.682726	0.183064
53	C	-4.313103	3.133672	0.555881
54	C	-3.766124	-3.517306	1.046911
55	C	-3.237576	-4.760368	0.392684
56	C	-6.529720	-2.017677	-1.557714
57	C	-7.828734	-2.755538	-1.365150
58	C	-7.349420	1.786071	-1.039200
59	C	-7.861992	2.488525	-2.265238
60	C	-6.387378	4.029355	1.346804
61	C	-7.366407	3.966224	2.486530
62	H	3.776593	-0.864069	-3.708695
63	H	1.535854	-2.030465	-4.824024
64	H	-0.512634	-3.326756	-3.247324
65	H	-1.077293	-1.750371	-3.869760
66	H	-1.169397	-2.124890	-2.134782
67	H	2.757146	0.122111	-0.161560
68	H	5.194183	-1.096303	-1.591529
69	H	5.023365	0.120074	1.207603
70	H	6.406594	1.419963	-1.180182
71	H	3.723287	2.217814	0.070950
72	H	5.172680	4.040059	-1.033030
73	H	4.916776	3.164162	-2.562937
74	H	4.657316	-4.233116	1.323168
75	H	4.505703	-5.305087	-0.101775
76	H	3.115521	-4.341561	0.474560
77	H	8.527374	-2.456564	0.877834
78	H	8.824009	-1.929436	2.557077
79	H	9.246431	-0.880831	1.175041
80	H	6.886905	4.534309	1.933787
81	H	8.601700	4.400915	1.468502
82	H	7.829747	3.164850	2.508574

83	H	1.319947	5.599650	-2.116627
84	H	1.125213	6.058984	-0.395413
85	H	0.683633	4.429981	-0.960951
86	H	-3.254351	-0.485797	3.636734
87	H	-0.912502	-1.113742	4.960335
88	H	1.765586	-1.755114	2.347661
89	H	1.318981	-2.209747	3.995157
90	H	1.756973	-0.520059	3.631171
91	H	-2.278249	-0.163570	-0.044087
92	H	-4.605636	-1.299995	1.613282
93	H	-4.523640	-0.647559	-1.374715
94	H	-5.996365	0.912033	0.802171
95	H	-3.444066	1.686586	-0.721756
96	H	-3.383708	3.554868	0.940885
97	H	-4.640425	3.700492	-0.313541
98	H	-3.654152	-4.872285	-0.610393
99	H	-3.483564	-5.625883	1.004471
100	H	-2.152432	-4.672343	0.291354
101	H	-7.727219	-3.488783	-0.561691
102	H	-8.105184	-3.256628	-2.290369
103	H	-8.614173	-2.058230	-1.065826
104	H	-7.629455	3.552346	-2.161402
105	H	-8.943432	2.376736	-2.324719
106	H	-7.383587	2.118078	-3.171436
107	H	-8.053576	3.138526	2.289191
108	H	-7.942744	4.889505	2.524196
109	H	-6.867319	3.782731	3.437400

Table S4. Bond lengths (Å) and angles (°)for isomers of [$NiBr_2(magi)_2$].

	syn-R[a]	*syn-R*[b]	*syn-S*[b]	*anti-S*[b]
Ni–Br	2.3052(9)	2.371	2.361	2.371
	2.2974(9)	2.359	2.358	2.367
Ni–C	1.904(4)	1.929	1.934	1.929
	1.890(4)	1.925	1.932	1.927
Br–Ni–Br	176.27(4)	174.05	178.40	179.64
C–Ni–C	177.3(2)	178.71	175.77	179.13
Br–Ni–C	89.88(15)	90.40	90.71	90.52
	88.67(15)	88.54	88.71	89.59
	90.20(14)	91.13	90.13	89.55
	91.40(15)	90.05	90.34	90.34
(Br_2C_2)[c]–(im)[d]	72.37(16)	72.29	72.64	71.00
	84.48(16)	77.62	76.84	71.26
(im)[d]–(im)[d]	–23.9(2)	–30.20	30.81	–37.91

[a] Obtained by crystallography. [b] Obtained from optimized structures by DFT calculations. [c] A plane defined by the coordinated atoms. [d] Planes defined by imidazolylidene rings.

Table 5. Calculated magnetic shielding (ppm) for protons in [$NiBr_2(magi)_2$]

Atom number	*syn-R*	*anti-S*	*syn-S*
62	25.4594	25.4059	25.4006
63	25.8587	25.7145	25.8718
64	27.2364	28.7271	27.5735
65	29.1405	28.5589	29.0168
66	28.1057	26.7361	27.2608
67	24.7010	25.1430	25.3407
68	26.9856	26.9410	26.9748
69	26.2734	26.4581	26.5902
70	27.1459	27.4615	27.4090
71	27.9161	28.3763	26.9792
72	27.7001	27.7828	27.8891
73	28.6921	28.7532	28.2927
74	30.6080	30.5042	30.5107
75	31.0006	30.9540	31.0481
76	29.4238	29.3592	30.0243
77	30.2250	30.2417	30.2751

78	30.6150	30.6400	30.6596
79	30.0943	30.2412	30.2964
80	30.1990	29.9282	30.0901
81	30.7231	30.6375	30.6111
82	29.2256	30.2310	30.1394
83	30.4835	30.4867	30.5554
84	30.8427	30.8353	29.6554
85	29.9452	29.8694	29.2177
86	25.4107	25.3740	25.3415
87	25.7755	25.7246	25.8507
88	27.2534	26.7472	27.3631
89	29.0145	28.8626	28.9502
90	27.6420	28.3999	27.3509
91	25.1263	24.9617	25.4463
92	26.7626	26.8492	26.9448
93	25.9261	26.5477	25.5495
94	27.0025	26.9862	26.9331
95	27.8277	28.3322	27.3498
96	28.5532	28.6105	28.2222
97	27.0448	27.1594	26.8804
98	30.2239	30.5133	30.5855
99	30.8216	30.9287	31.0752
100	29.6813	29.3696	29.9354
101	30.2148	30.2466	30.2969
102	30.8292	30.6876	30.7787
103	30.2680	30.2249	30.2788
104	29.9273	29.9834	29.9185
105	30.6621	30.6530	30.6378
106	30.4284	30.4617	30.4580
107	29.8650	29.9092	29.8585
108	30.6337	30.6315	30.6018
109	30.4364	30.4414	30.3850

Table 6. Observed and calculated ^{1}H NMR chemical shifts (ppm) for isomers of [$NiBr_2(magi)_2$]

	observed		calculated		
	syn	*anti*	*syn-R*	*anti-S*	*syn-S*
1-Glc	7.80	7.60	7.788	7.641	7.277
5-Im	7.03	7.03	7.233	7.281	7.301
4-Im	6.81	6.81	6.826	6.930	6.779
3-Glc	5.88	5.66	6.525	6.095	6.557
2-Glc	5.47	5.48	5.700	5.677	5.609
4-Glc	5.32	5.25	5.487	5.327	5.384
Me-Im	4.38	4.43	4.431	4.495	4.586
6-Glc	4.34	4.25	5.169	5.064	5.156
5-Glc	4.27	4.12	4.637	4.123	5.390
6-Glc	4.13	4.12	3.837	3.774	4.226
4-Ac	2.13	2.09	2.163	2.033	2.040
2-Ac	2.05	2.08	2.057	2.080	1.805
6-Ac	2.034	2.028	1.978	1.984	2.321
3-Ac	2.01	2.028	1.971	1.964	1.911

[a] Scaled using calculated magnetic shielding values (25.4096 and 32.2243) and observed chemical shifts (7.26 and 0.00) for chloroform and tetramethylsilane, respectively.