Supporting Information to the Paper

Coordination reactions of 2-pyridinecarboxaldehyde-phenylhydrazonatolithium with selected transition metal (Zn, Sn, Fe, Co, Ni and Zr) chlorides and its coupling reaction with dichloromethane

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Table S1 Selected bond lengths (Å) and angles (°) for **1**, **3**, **4** and **7**

Complexes	**1**	**3**	**4**	**7**			
M-N1	2.028(4)	2.0480(17)	1.993(3)	Ni1-N1	1.968(2)	Ni1-N4	1.978(2)
M-N3	1.950(3)	1.9825(16)	1.946(3)	Ni1-N3	1.914(2)	Ni1-N6	1.927(2)
N1-C2	1.352(6)	1.351(3)	1.353(5)	N1-C2	1.361(3)	N(4)-C(14)	1.353(3)
C2-C1	1.427(6)	1.439(3)	1.435(5)	C2-C1	1.439(4)	C(13)-C(14)	1.446(4)
C1-N2	1.307(6)	1.295(3)	1.296(5)	C1-N2	1.302(4)	N(5)-C(13)	1.301(3)
N2-N3	1.348(5)	1.349(2)	1.346(4)	N2-N3	1.347(3)	N(5)-N(6)	1.345(3)
N3-C7	1.403(5)	1.409(3)	1.409(4)	N3-C7	1.417(3)	N(6)-C(19)	1.414(3)
N1-C6	1.334(6)	1.349(3)	1.344(5)	N1-C6	1.357(4)	N(4)-C(18)	1.347(3)
C2-C3	1.415(6)	1.400(3)	1.394(5)	C2-C3	1.408(4)	C(14)-C(15)	1.401(4)
C3-C4	1.368(7)	1.366(3)	1.356(6)	C3-C4	1.366(4)	C(15)-C(16)	1.377(4)
C4-C5	1.384(8)	1.375(4)	1.380(6)	C4-C5	1.395(4)	C(16)-C(17)	1.383(5)
C5-C6	1.398(7)	1.363(3)	1.356(6)	C5-C6	1.365(4)	C(17)-C(18)	1.373(4)
M-N1-C2	122.0(3)	124.06(14)	122.3(2)	Ni1-N1-C2	123.73(19)	Ni1-N4-C14	123.49(18)
N1-C2-C1	122.0(4)	120.86(18)	120.8(3)	N1-C2-C1	121.0(2)	N4-C14-C13	120.8(2)
C2-C1-N2	133.0(4)	133.50(19)	133.7(4)	C2-C1-N2	132.0(2)	C14-C13-N5	132.0(2)
C1-N2-N3	123.0(4)	122.45(17)	122.7(3)	C1-N2-N3	121.0(2)	C13-N5-N6	120.9(2)
N2-N3-M	125.1(3)	126.80(13)	124.4(2)	N2-N3-Ni1	127.95(18)	N5-N6-Ni1	127.76(16)
N1-M-N3	94.84(15)	92.33(7)	95.47(12)	N1-Ni1-N3	93.80(9)	N4-Ni1-N6	93.04(9)
N2-N3-C7	111.6(3)	111.68(15)	111.5(3)	N2-N3-C7	112.6(2)	N5-N6-C19	111.9(2)
M-N3-C7	123.3(3)	121.52(12)	123.9(2)	Ni1-N3-C7	119.38(16)	Ni1-N6-C19	120.22(16)

Table S2 Selected bond lengths (Å) and angles (°) for **2**

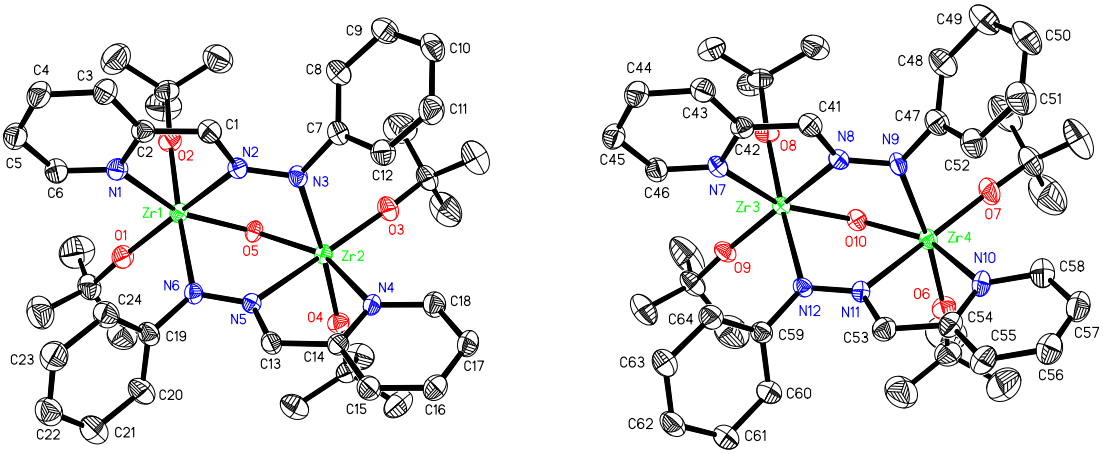
Sn1-N1	2.375(3)	Sn1-N4	2.395(3)
Sn1-N3	2.186(3)	Sn1-N6	2.207(3)
N1-C2	1.354(4)	N4-C14	1.346(4)
C2-C1	1.447(5)	C13-C14	1.439(5)
C1-N2	1.297(4)	C13-N5	1.306(5)
N2-N3	1.354(4)	N5-N6	1.340(4)
N3-C7	1.419(5)	N6-C19	1.430(4)
N1-C6	1.343(4)	N4-C18	1.343(5)
C2-C3	1.401(5)	C14-C15	1.405(5)
C3-C4	1.371(5)	C15-C16	1.355(6)
C4-C5	1.381(6)	C16-C17	1.374(6)
C5-C6	1.378(5)	C17-C18	1.382(6)
Sn1-N1-C2	123.11(19)	N1-Sn1-N4	148.07(9)
N1-C2-C1	120.6(3)	Sn1-N4-C14	124.5(2)
C2-C1-N2	131.1(3)	N4-C14-C13	121.0(3)
C1-N2-N3	120.6(3)	C14-C13-N5	132.1(3)
N2-N3-Sn1	127.5(2)	C13-N5-N6	121.9(3)
N1-Sn1-N3	75.86(10)	N5-N6-Sn1	128.7(2)
N4-Sn1-N6	77.26(10)	N2-N3-C7	112.0(3)
N3-Sn1-N4	82.37(10)	Sn1-N3-C7	116.7(2)
N1-Sn1-N6	81.61(9)	N5-N6-C19	110.8(3)
N3-Sn1-N6	94.94(10)	Sn1-N6-C19	116.8(2)

Table S3 Selected bond lengths (Å) and angles (°) for **5**

Zr1-N6	2.322(5)	Zr2-N3	2.325(5)
Zr1-N1	2.375(5)	Zr2-N4	2.382(6)
Zr1-N2	2.438(5)	Zr2-N5	2.440(5)
Zr1-O2	1.932(4)	Zr2-O4	1.936(4)
Zr1-O1	1.941(5)	Zr2-O3	1.949(4)
Zr1-O5	1.957(4)	Zr2-O5	1.963(4)
N1-C2	1.358(9)	N4-C14	1.332(8)
C1-C2	1.419(10)	C13-C14	1.442(9)
N2-C1	1.313(8)	N5-C13	1.305(8)
N2-N3	1.349(7)	N5-N6	1.346(7)
N3-C7	1.446(8)	N6-C19	1.441(8)
Zr3-N12	2.349(5)	Zr4-N9	2.353(6)
Zr3-N7	2.375(6)	Zr4-N10	2.382(5)
Zr3-N8	2.437(5)	Zr4-N11	2.429(5)
Zr3-O8	1.946(4)	Zr4-O6	1.924(5)
Zr3-O9	1.933(4)	Zr4-O7	1.922(5)
Zr3-O10	1.960(5)	Zr4-O10	1.961(4)
N7-C42	1.357(8)	N10-C54	1.351(9)
C41-C42	1.454(10)	C53-C54	1.438(10)
N8-C41	1.291(9)	N11-C53	1.323(9)
N8-N9	1.320(7)	N11-N12	1.324(7)
N9-C47	1.432(8)	N12-C59	1.443(8)
N1-Zr1-N2	67.22(18)	N4-Zr2-N5	67.17(18)
O5-Zr1-N2	81.34(18)	O5-Zr2-N5	81.74(17)
O1-Zr1-O5	110.9(2)	O3-Zr2-O5	111.8(2)
O1-Zr1-N1	99.0(2)	O3-Zr2-N4	97.7(2)
O2-Zr1-N6	168.2(2)	O4-Zr2-N3	170.1(2)
N2-N3-C7	117.1(5)	N5-N6-C19	116.8(5)
N2-N3-Zr2	114.8(4)	N5-N6-Zr1	114.6(4)
N7-Zr3-N8	83.81(19)	N10-Zr4-N11	67.63(18)
O10-Zr3-N8	99.06(19)	O10-Zr4-N11	81.99(17)
O9-Zr3-O10	112.1(2)	O7-Zr4-O10	112.0(2)
O9-Zr3-N7	96.8(2)	O7-Zr4-N10	96.3(2)
O8-Zr3-N12	168.84(18)	O6-Zr4-N9	166.8(2)
N8-N9-C47	118.1(5)	N11-N12-C59	118.1(5)
N8-N9-Zr4	115.0(3)	N11-N12-Zr3	113.4(4)

Table S**4** Selected bond lengths (Å) and angles (°) from X-Ray crystallography and B3LYP calculations for **6**

	X-ray	B3LYP		X-ray	B3LYP
N2-C1	1.293(3)	1.2998	N2-N3	1.344(3)	1.3298
C1-C2	1.473(4)	1.4789	N3-C7	1.397(3)	1.399
N1-C2	1.348(3)	1.3492	C1-C13	1.509(3)	1.5271
N2-C1-C13	124.6(2)	124.9794	C2-C1-C13	121.0(2)	119.7043
N2-C1-C2	114.4(3)	115.0978	C1-N2-N3	119.5(3)	121.2654
N2-N3-C7	118.8(3)	120.153	C1A-C13-C1	117.1(3)	118.2973
N1-C2-C1	117.2(3)	117.2665	C8-C7-N3	121.9(3)	122.1844
C3-C2-C1	121.6(3)	121.7238	C12-C7-N3	118.5(3)	118.4751



(**a**) (**b**)

Fig. S1 Molecular structure of complex **5** (two similar independent molecules exist in the unit cell, as shown in the (**a**) and (**b**), respectively) with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

Table S5 Standard orientation of optimized **6**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000046	0.000100	-1.556004
2	1	0	-0.841512	-0.258874	-2.206549
3	1	0	0.841380	0.259076	-2.206608
4	6	0	0.375654	-1.255970	-0.772908
5	6	0	-0.547861	-2.410921	-0.753264
6	6	0	-0.121598	-3.694656	-0.353425
7	6	0	-2.668075	-3.229647	-1.206741
8	6	0	-1.018333	-4.750137	-0.393412
9	1	0	0.903231	-3.832140	-0.034199
10	6	0	-2.325916	-4.524523	-0.838417
11	1	0	-3.673737	-3.000738	-1.554346
12	1	0	-0.702787	-5.744887	-0.092058
13	1	0	-3.054579	-5.325764	-0.896511
14	7	0	1.516665	-1.452316	-0.182111
15	7	0	2.467877	-0.523017	-0.191739
16	1	0	2.317442	0.394909	-0.636184
17	6	0	3.680174	-0.751593	0.467991
18	6	0	4.661081	0.253182	0.433760
19	6	0	3.943332	-1.946809	1.156079
20	6	0	5.882820	0.060620	1.073105
21	1	0	4.458749	1.182504	-0.089216
22	6	0	5.170640	-2.123731	1.789093
23	1	0	3.181941	-2.715438	1.189369
24	6	0	6.149896	-1.128146	1.754388
25	1	0	6.630119	0.848336	1.037510
26	1	0	5.361663	-3.053026	2.318739
27	1	0	7.103343	-1.275595	2.251683
28	6	0	-0.375681	1.256149	-0.772847
29	6	0	0.547891	2.411017	-0.753106
30	6	0	0.121657	3.694825	-0.353483
31	6	0	2.668192	3.229557	-1.206505
32	6	0	1.018464	4.750242	-0.393523
33	1	0	-0.903187	3.832433	-0.034357
34	6	0	2.326071	4.524501	-0.838375
35	1	0	3.673882	3.000521	-1.553930
36	1	0	0.702951	5.745050	-0.092324
37	1	0	3.054753	5.325718	-0.896549
38	7	0	-1.516691	1.452520	-0.182044
39	7	0	-2.467861	0.523199	-0.191672
40	1	0	-2.317441	-0.394633	-0.636242

41	6	0	-3.680196	0.751623	0.468037
42	6	0	-3.943505	1.946749	1.156223
43	6	0	-4.661019	-0.253234	0.433668
44	6	0	-5.170866	2.123495	1.789185
45	1	0	-3.182200	2.715459	1.189627
46	6	0	-5.882795	-0.060862	1.072981
47	1	0	-4.458562	-1.182504	-0.089362
48	6	0	-6.150023	1.127823	1.754364
49	1	0	-5.361994	3.052736	2.318893
50	1	0	-6.629997	-0.848665	1.037291
51	1	0	-7.103485	1.275123	2.251671
52	7	0	-1.815135	-2.196095	-1.163317
53	7	0	1.815183	2.196063	-1.163050

Table S6 Standard orientation of optimized azo isomer **b1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.006387	0.046199	2.530291
2	1	0	-0.755991	-0.400900	3.192750
3	1	0	0.745826	0.524638	3.166197
4	6	0	0.715848	-1.113691	1.804889
5	1	0	1.083201	-1.749794	2.624111
6	6	0	-0.724117	1.177086	1.757110
7	1	0	-1.067034	1.857190	2.549749
8	6	0	-0.154948	-1.996235	0.922290
9	6	0	-0.545947	-3.265203	1.362902
10	6	0	-1.311214	-2.267758	-1.046216
11	6	0	-1.360630	-4.048385	0.547246
12	1	0	-0.212663	-3.632775	2.328775
13	6	0	-1.753947	-3.542261	-0.688666
14	1	0	-1.597831	-1.834944	-2.002553
15	1	0	-1.675585	-5.036585	0.870029
16	1	0	-2.384887	-4.113467	-1.361806
17	6	0	0.163940	2.040433	0.871379
18	6	0	0.531176	1.673904	-0.429882
19	6	0	1.364477	2.523385	-1.150645
20	1	0	0.175478	0.736043	-0.841390
21	6	0	1.389832	3.981294	0.743931
22	6	0	1.806261	3.706818	-0.556367
23	1	0	1.667207	2.265050	-2.161434
24	1	0	1.710583	4.892905	1.245769
25	1	0	2.454450	4.399030	-1.084862
26	7	0	1.963616	-0.604713	1.180110
27	7	0	2.425395	-1.360383	0.299747
28	7	0	-1.983608	0.657253	1.177818
29	7	0	-2.409269	1.312321	0.205030
30	6	0	-3.660888	0.859789	-0.318624
31	6	0	-4.372887	-0.251102	0.159435
32	6	0	-4.167482	1.611166	-1.383944
33	6	0	-5.583785	-0.595322	-0.431499
34	1	0	-3.960661	-0.819227	0.985310
35	6	0	-5.383237	1.262334	-1.971575
36	1	0	-3.591216	2.463222	-1.730091
37	6	0	-6.092635	0.158858	-1.496039
38	1	0	-6.138511	-1.454134	-0.063937
39	1	0	-5.775220	1.849094	-2.796971
40	1	0	-7.039784	-0.116280	-1.951134

41	6	0	3.652280	-0.917584	-0.282532
42	6	0	4.259771	0.319488	-0.016246
43	6	0	4.241225	-1.810243	-1.184355
44	6	0	5.454648	0.644248	-0.649241
45	1	0	3.780090	1.000387	0.676863
46	6	0	5.441658	-1.480350	-1.812181
47	1	0	3.740389	-2.754226	-1.374010
48	6	0	6.049242	-0.252716	-1.545139
49	1	0	5.927729	1.601252	-0.448345
50	1	0	5.899402	-2.176336	-2.508752
51	1	0	6.982499	0.009818	-2.035028
52	7	0	0.583286	3.176864	1.449394
53	7	0	-0.533847	-1.509180	-0.268837

Table S7 Standard orientation of optimized azo isomer **b2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.364136	0.883111	1.464172
2	1	0	1.012756	1.734206	1.694450
3	1	0	0.432735	0.175561	2.295339
4	6	0	-1.089510	1.402203	1.377697
5	1	0	-1.357253	1.688836	2.405156
6	6	0	0.922253	0.194271	0.201786
7	6	0	-1.285032	2.629978	0.500011
8	6	0	-1.850342	3.795382	1.030655
9	6	0	-1.059945	3.622337	-1.563528
10	6	0	-2.017284	4.908022	0.209062
11	1	0	-2.155669	3.825265	2.072231
12	6	0	-1.615320	4.823499	-1.121846
13	1	0	-0.729761	3.516845	-2.595507
14	1	0	-2.453751	5.822152	0.601204
15	1	0	-1.724646	5.661924	-1.802131
16	6	0	0.531274	-1.268335	0.079008
17	6	0	0.060317	-1.786246	-1.132242
18	6	0	-0.252901	-3.141076	-1.214288
19	1	0	-0.060233	-1.132489	-1.990328
20	6	0	0.395230	-3.330933	1.079931
21	6	0	-0.079607	-3.937798	-0.084267
22	1	0	-0.624982	-3.565784	-2.142286
23	1	0	0.541664	-3.919643	1.984529
24	1	0	-0.307158	-4.999094	-0.098231
25	7	0	-1.993204	0.260136	1.094268
26	7	0	-2.948073	0.534546	0.337752
27	6	0	-3.837936	-0.555655	0.082671
28	6	0	-3.647636	-1.866157	0.547158
29	6	0	-4.956365	-0.241386	-0.696069
30	6	0	-4.583237	-2.845386	0.231758
31	1	0	-2.769510	-2.090085	1.141585
32	6	0	-5.892562	-1.227279	-1.006116
33	1	0	-5.069297	0.780437	-1.043980
34	6	0	-5.706791	-2.530081	-0.542229
35	1	0	-4.439653	-3.861760	0.587337
36	1	0	-6.761799	-0.980568	-1.608411
37	1	0	-6.432404	-3.301584	-0.783482
38	7	0	0.693307	-2.032165	1.170690
39	7	0	-0.896192	2.549982	-0.783388
40	7	0	2.390310	0.442977	0.198283

41	7	0	3.086697	-0.536467	-0.136224
42	1	0	0.556265	0.749663	-0.670475
43	6	0	4.495295	-0.282347	-0.171824
44	6	0	5.090610	0.958579	0.100423
45	6	0	5.290458	-1.381552	-0.510100
46	6	0	6.473723	1.085335	0.032845
47	1	0	4.454527	1.797204	0.359554
48	6	0	6.677337	-1.249159	-0.575670
49	1	0	4.798150	-2.326913	-0.714429
50	6	0	7.270368	-0.015765	-0.304359
51	1	0	6.938442	2.044670	0.242633
52	1	0	7.292386	-2.105033	-0.837347
53	1	0	8.350078	0.091747	-0.354904

Table S8 Standard orientation of optimized azo isomer **b3**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.221911	-0.020019	-0.158547
2	1	0	0.270482	-0.392917	-1.186001
3	1	0	0.272157	-0.885262	0.505505
4	6	0	1.424836	0.899086	0.128631
5	6	0	-1.133917	0.678185	0.050481
6	6	0	1.573734	2.016204	-0.897933
7	6	0	2.350998	1.848052	-2.051159
8	6	0	0.969373	4.138105	-1.545650
9	6	0	2.426493	2.890102	-2.971356
10	1	0	2.888340	0.920256	-2.211965
11	6	0	1.721710	4.065825	-2.716863
12	1	0	0.403062	5.037543	-1.310329
13	1	0	3.026739	2.786472	-3.870717
14	1	0	1.752632	4.905466	-3.403647
15	6	0	-1.430457	0.980242	1.510491
16	6	0	-1.929306	2.228201	1.898827
17	6	0	-2.207963	2.456737	3.244417
18	1	0	-2.082394	3.004282	1.156051
19	6	0	-1.468728	0.224229	3.679207
20	6	0	-1.978484	1.431260	4.159541
21	1	0	-2.593621	3.417966	3.572129
22	1	0	-1.265889	-0.597466	4.364345
23	1	0	-2.178935	1.560994	5.218365
24	7	0	-1.196098	-0.005102	2.391322
25	7	0	0.892248	3.146801	-0.648628
26	7	0	-2.151426	-0.154122	-0.645050
27	7	0	-3.196675	-0.352998	0.006547
28	1	0	-1.136130	1.622608	-0.508916
29	6	0	-4.182623	-1.137508	-0.673237
30	6	0	-4.029907	-1.670721	-1.961976
31	6	0	-5.363392	-1.359735	0.041808
32	6	0	-5.060156	-2.418772	-2.520952
33	1	0	-3.105236	-1.487428	-2.497188
34	6	0	-6.393947	-2.110174	-0.523946
35	1	0	-5.447785	-0.935503	1.037161
36	6	0	-6.243445	-2.640357	-1.805676
37	1	0	-4.945664	-2.833718	-3.518423
38	1	0	-7.309892	-2.281191	0.033736
39	1	0	-7.043325	-3.225990	-2.249587
40	7	0	2.735775	0.225234	0.258507

41	7	0	2.706702	-1.007801	0.060216
42	6	0	3.969868	-1.666125	0.195897
43	6	0	3.952240	-3.044313	-0.040548
44	6	0	5.169674	-1.024648	0.539678
45	6	0	5.128638	-3.786263	0.062081
46	1	0	3.006875	-3.509483	-0.300925
47	6	0	6.339134	-1.769815	0.640947
48	1	0	5.158341	0.043979	0.721216
49	6	0	6.322618	-3.149748	0.402729
50	1	0	5.113069	-4.856317	-0.121498
51	1	0	7.270451	-1.278476	0.907847
52	1	0	7.240644	-3.724364	0.485072
53	1	0	1.278987	1.396287	1.096023
