ELECTRONIC SUPPORTING INFORMATION

for

Structural studies of Group 1 metal 4-azapentalenyl complexes

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Synthesis of **5**.

Potassium metal (0.50 g, 13 mmol) was added to **4** (1.0 g, 6.4 mmol) in thf (50 mL) and stirred at 25 ^{o}C for 3 hours. The red solution was filtered, to remove excess potassium metal and other impurities, and then concentrated *in vacuo* to *ca.* 10 mL. Upon cooling to -25 ^{o}C for a week red, crystals of **5** formed (1.36 g, 93%). Anal. Calcd. for $C_{11}H_8NK(C_4H_8O)_{1/2}$: C, 67.71; H, 5.25; N, 6.08. Found: C, 67.68; H, 5.29; N, 6.08 %. ^{1}H NMR (thf-d^{8}, 299.898 MHz, 298K, ppm): δ 1.78 (m, 2H, CH_2), 3.62 (m, 2H, OCH_2), 5.85 (m, 1H, CH), 5.97 (m, 1H, CH), 6.27 (m, b, 1H, C), 6.58 (m, 1H, CH), 6.71 (m, 1H, CH), 6.76 (m, 1H, CH), 6.71 (m, 1H, CH), 7.35 (m, 1H, CH). ^{13}C{^{1}H} NMR (thf-d^{8}, 75.4 MHz, 298K, ppm): δ 83.3 (CH), 83.9 (CH), 98.1 (CH), 105.0 (CH), 109.6 (CH), 110.9 (C), 111.2 (CH), 118.9 (CH), 120.5 (CH), 131.3 (C), 132.2 (C). (resonances for thf not detected by ^{13}C {^{1}H} NMR due to overlap with thf-d^{8} resonances).

Synthesis of **6**.

Potassium metal (0.25 g, 6.4 mmol) was added to **4** (0.52 g, 3.3 mmol) in thf (50 mL) and stirred 25 ^{o}C at for 12 hours. The red solution was filtered, to remove excess potassium metal and other impurities, and the solvent was removed *in vacuo*. Neat tmen (20 mL) was added and the mixture stirred at ambient temperature for 2 hours, after which time the red solution was filtered from impurities and concentrated *in vacuo* to *ca*. 15 mL. Upon cooling to – 25 ^{o}C for a week, red crystals of **6** formed. Anal. Calcd. for $C_{11}H_8NK(C_6H_{16}N_2)$: C, 65.97; H, 7.82; N, 13.58. Found: C, 66.08; H, 7.58; N, 13.24%. ^{1}H NMR (py-d^5, 300.132 MHz, 300K, ppm): δ 2.16 (s, 12H, CH_3), 2.35 (s, 4H, CH_2), 6.56 (m, 1H, CH), 6.62 (m, 1H, CH), 6.93 (m, 1H, CH), 7.16 (m, 1H, CH), 7.44 (m, 2H, CH), 7.46 (m, 1H, CH), 8.00 (m, 1H, CH). ^{13}C{^{1}H} NMR (py-d^5, 75.4677 MHz, 300K, ppm): δ 46.0 (CH_3), 58.2 (CH_2), 84.32 (CH), 85.0 (CH), 99.0 (CH), 105.1 (CH), 109.9 (CH), 110.2 (C), 111.4 (CH), 119.4 (CH), 120.6 (CH), 131.5 (C), 132.0 (C).

Computational details

Full geometry optimisations were carried out with the use of the B3LYP density functional level of theory combined with the 6-31+G(d) basis set. Vibrational frequency calculations at this level of theory confirmed that all the species studied were true minima. Single-point energies on these optimised geometries were calculated at the B3LYP level with the 6-311+G(d,p) basis set. The energies quoted in this paper refer to this final level of theory. All calculations were carried out with the Gaussian 98[1] program.

1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; C, S. M.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Otcherski, J.; Petersson, G. A.; Ayala, P. J.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuk, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomberts, R.; Martin, R. L.; Fox, D. J.; Kieth, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98 A.1, Revision A.1*; Gaussian, Inc.: Pittsburgh, PA, 1998.

Total Energies (Hartree) for structures **7-12**

Compound	B3LYP/6-31+G(d)[a]	B3LYP/6-311+G(d,p)[b]
C_7H_6NLi (**7a**)	-332.623446	-332.6994
C_7H_6NLi (**8a**)	-332.616210	-332.6914
C_7H_6NNa (**8b**)	-487.383003	-487.4619
C_7H_6NK (**8c**)	-925.004198	-925.1183
$C_{11}H_8NLi$ (**9a**)	-486.271562	-486.3768
$C_{11}H_8NLi$ (**11a**)	-486.271610	-486.3764
$C_{11}H_8NLi$ (**12a**)	-486.269481	-486.3751
$C_{11}H_8NNa$ (**10b**)	-641.035319	-641.1433
$C_{11}H_8NNa$ (**12b**)	-641.031037	-641.1398
$C_{11}H_8NK$ (**10c**)	-1078.656833	-1078.7994

[a] Geometry optimised at this level of theory.

[b] Single point energy on geometry optimised at B3LYP/6-31+G(d).

Optimised B3LYP/6-31+G(d) Gas-Phase Geometries (Å) for structures **7-12**

7a

C	0.065394	0.757168	-0.107318
N	0.062476	-0.661486	-0.092161
C	-1.260165	-1.147176	-0.096394
C	1.366458	-1.134369	-0.037228
C	-2.096552	-0.016780	-0.183986
C	2.195038	-0.014658	-0.003488
C	-1.312844	1.165612	-0.131879
C	1.412290	1.166660	-0.029665
H	-1.479076	-2.197436	-0.218209
H	1.587433	-2.191528	-0.043657
H	-3.177259	-0.060313	-0.250852
H	3.277437	-0.055021	0.029534
H	-1.674834	2.181882	-0.205061
H	1.772053	2.186397	-0.028413
Li	-0.986933	0.035893	1.633841

8a

C	0.509355	-0.617281	0.000000
N	0.000000	0.706276	0.000000
C	-0.360135	1.079241	1.306460
C	-0.360135	1.079241	-1.306460
C	-0.016190	0.001851	2.132870
C	-0.016190	0.001851	-2.132870
C	0.497962	-1.062668	1.353481
C	0.497962	-1.062668	-1.353481
H	-0.670961	2.086398	1.542085
H	-0.670961	2.086398	-1.542085
H	-0.113818	0.005661	3.212375
H	-0.113818	0.005661	-3.212375
H	0.834972	-2.025920	1.710864
H	0.834972	-2.025920	-1.710864
Li	-1.538718	-0.531202	0.000000

8b

C	0.844043	-0.310583	0.000000
N	0.000000	0.823571	0.000000
C	-0.420382	1.108847	1.305963
C	-0.420382	1.108847	-1.305963
C	0.205062	0.171454	2.137246
C	0.205062	0.171454	-2.137246
C	0.969329	-0.732568	1.354636
C	0.969329	-0.732568	-1.354636
H	-0.974426	2.006727	1.539712
H	-0.974426	2.006727	-1.539712
H	0.140590	0.174410	3.219650
H	0.140590	0.174410	-3.219650
H	1.582950	-1.546247	1.717921
H	1.582950	-1.546247	-1.717921
Na	-1.419144	-1.067643	0.000000

8c

C	1.067926	0.075802	0.000000
N	0.000000	0.996778	0.000000
C	-0.453468	1.205891	1.306902
C	-0.453468	1.205891	-1.306902
C	0.376795	0.445171	2.140909
C	0.376795	0.445171	-2.140909
C	1.306253	-0.283755	1.356089
C	1.306253	-0.283755	-1.356089
H	-1.175307	1.976049	1.540633
H	-1.175307	1.976049	-1.540633
H	0.330913	0.455096	3.224438
H	0.330913	0.455096	-3.224438
H	2.092924	-0.932397	1.719088
H	2.092924	-0.932397	-1.719088
K	-1.245241	-1.412497	0.000000

9a

C	0.000000	0.000000	0.000000
N	0.000000	0.000000	1.414374
C	1.296041	0.000000	1.920299
C	2.157023	-0.004442	0.809461
C	1.365305	0.010328	-0.407655
C	-1.365450	0.057007	-0.419348
C	-2.159234	0.051855	0.755327
C	-1.314945	0.062427	1.888304
C	3.574570	-0.015978	0.696023
C	4.155698	-0.008097	-0.557980
C	3.372435	0.009051	-1.744956
C	1.988457	0.014914	-1.671337
H	-1.722728	0.023573	-1.439376
H	-3.241573	0.046613	0.794951
H	-1.544964	-0.029716	2.939346
H	1.488440	-0.046227	2.981470
H	4.194238	-0.033707	1.590075
H	5.240273	-0.018794	-0.642568
H	3.865985	0.009718	-2.713242
H	1.388792	0.016317	-2.579758
Li	-0.922215	1.800974	0.728711

11a

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.408021
C	1.355852	0.000000	-0.402368
C	2.173908	-0.023844	0.730919
C	-0.808842	-0.013015	2.605312
C	1.443014	-0.176178	3.246307
C	0.107350	-0.050641	3.732577
C	-2.202192	0.021044	2.816910
C	-2.696225	0.032035	4.114783
C	-1.807650	0.011448	5.219083
C	-0.433489	-0.033502	5.046615
N	1.344534	-0.028527	1.830396
H	2.370528	0.047278	3.753581
H	3.249486	-0.030046	0.832502
H	1.716811	0.024509	-1.423309
H	-0.869750	0.029289	-0.642053
H	-3.768305	0.068941	4.287220
H	-2.880964	0.059072	1.967664
H	0.230003	-0.041042	5.908525
H	-2.215416	0.037637	6.227030
Li	0.442488	-1.833461	2.521645

12a

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.412467
C	1.324860	0.000000	-0.455126
C	1.347154	0.000584	1.810507
N	2.131866	0.000880	0.649090
C	2.252275	0.005062	2.917154
C	3.502439	-0.008372	0.948612
C	3.622003	0.004849	2.327388
C	2.080082	0.007343	4.305269
C	3.201689	-0.040057	5.167929
C	4.515752	-0.033667	4.613816
C	4.733876	-0.031147	3.233581
H	1.729482	0.004382	-1.457080
H	-0.874330	0.004046	-0.639232
H	-0.865384	0.008894	2.061722
H	4.251877	-0.000316	0.171336
H	1.077773	0.014316	4.728262
H	5.750596	-0.040016	2.848352
H	5.371475	-0.055762	5.283869
H	3.064434	-0.033116	6.244010
Li	3.376576	-1.711750	3.818670

10b

C	0.000000	0.000000	0.000000
N	0.000000	0.000000	1.401789
C	1.334476	0.000000	1.918255
C	2.166784	0.239085	0.781039
C	1.364346	0.192353	-0.421724
C	-1.275595	-0.425705	-0.425504
C	-2.050939	-0.619033	0.751086
C	-1.250873	-0.360489	1.867379
C	3.559348	0.467661	0.654840
C	4.121473	0.584994	-0.609571
C	3.336228	0.490281	-1.782908
C	1.959783	0.299784	-1.688862
H	-1.619662	-0.507832	-1.447995
H	-3.103243	-0.874858	0.786108
H	-1.476596	-0.384358	2.924145
H	1.505485	0.348480	2.929474
H	4.184132	0.545064	1.542409
H	5.191579	0.758981	-0.701089
H	3.807482	0.585631	-2.757482
H	1.347708	0.256761	-2.587904
Na	0.723137	-2.219870	0.894003

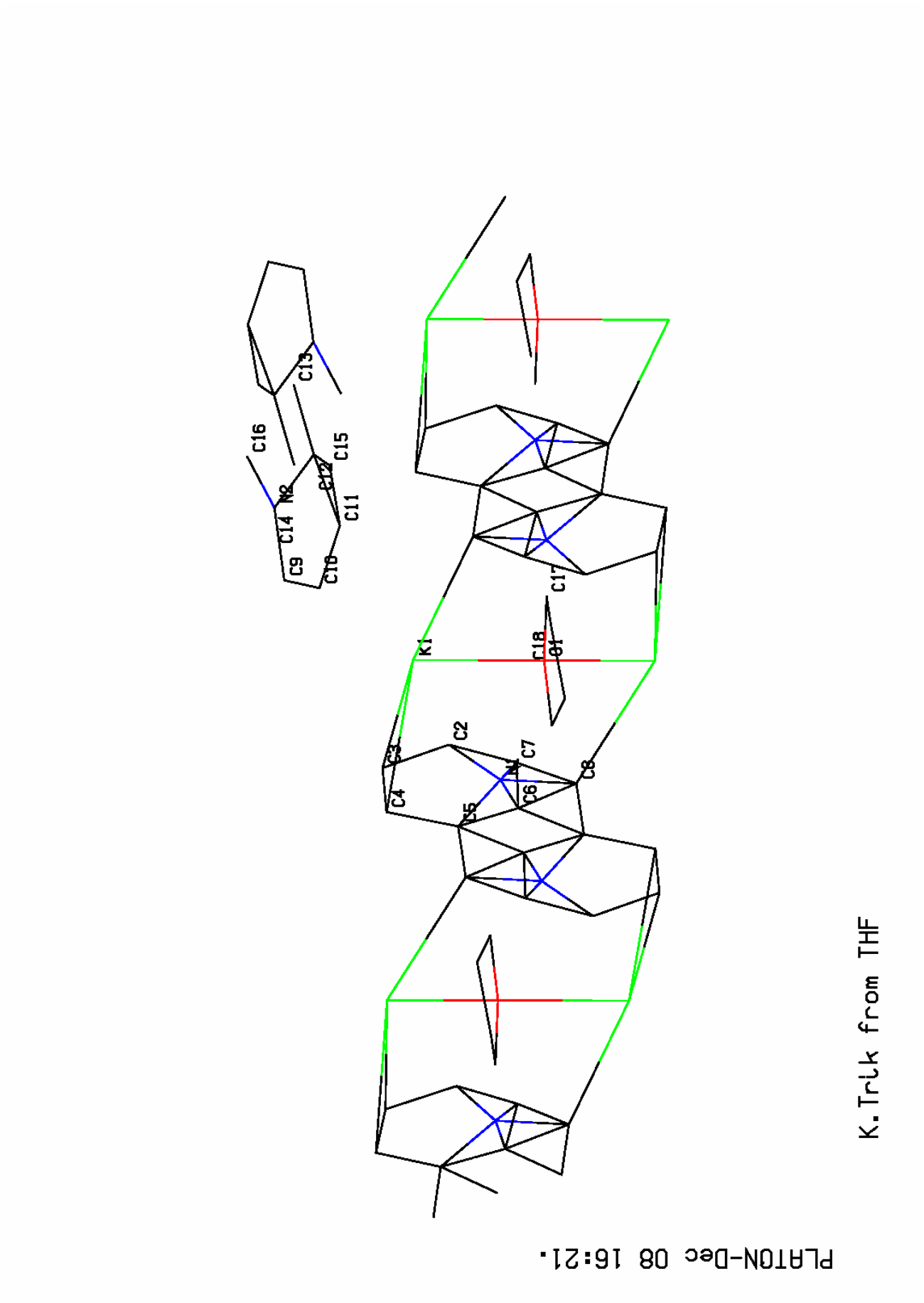
12b

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.413654
C	1.324051	0.000000	-0.455483
C	1.348759	0.007170	1.812710
N	2.132659	0.001832	0.650848
C	2.254956	-0.012380	2.920753
C	3.503410	-0.044913	0.951101
C	3.619169	-0.021204	2.338208
C	2.079157	-0.085294	4.307946
C	3.195872	-0.187308	5.163074
C	4.509298	-0.144451	4.614704
C	4.731297	-0.055588	3.240656
H	4.253405	0.021887	0.176608
H	1.729097	0.004710	-1.457345
H	-0.874586	0.010743	-0.639205
H	-0.865425	0.018327	2.062943
H	5.748214	-0.008359	2.855916
H	1.075445	-0.070555	4.729893
H	3.057853	-0.218093	6.239853
H	5.363603	-0.164545	5.288324
Na	3.298826	-2.253942	3.465584

10c

C	0.000000	0.000000	0.000000
N	0.000000	0.000000	1.401644
C	1.318408	0.000000	1.918950
C	2.169727	0.142528	0.795056
C	1.370975	0.100246	-0.416494
C	-1.307663	-0.325380	-0.427419
C	-2.089147	-0.481133	0.746291
C	-1.269570	-0.295073	1.867777
C	3.577343	0.285956	0.669671
C	4.151587	0.332876	-0.591940
C	3.367908	0.250818	-1.770389
C	1.982901	0.141991	-1.681229
H	-1.658661	-0.369562	-1.450136
H	-3.157053	-0.662617	0.783107
H	-1.506228	-0.273925	2.922555
H	1.499296	0.283977	2.947224
H	4.200939	0.356496	1.558969
H	5.230618	0.442334	-0.681003
H	3.849917	0.293530	-2.743601
H	1.375632	0.111217	-2.584567
K	0.502124	-2.623443	0.838456

Atom labelling diagram for the crystal structure of **5**



Atom labelling diagram for the crystal structure of **6**