Supporting Information

The Aluminyl Anion: A New Generation of Aluminium Nucleophile
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anie_202007530_sm_miscellaneous_information.pdf
Contents:

(i) Computational details  
(ii) Xyz coordinates of optimised anions  
(iii) References
Computational details

The geometry optimisations were performed with the Gaussian16 (Revision C.01) programme\textsuperscript{1} using the PBE1PBE hybrid exchange functional\textsuperscript{2} and Def2-TZVP basis set.\textsuperscript{3} In addition, Grimme’s empirical dispersion correction with Becke-Johnson damping (GD3BJ)\textsuperscript{4} was used as well as an ultrafine integration grid. Full analytical frequency calculations were performed for the optimized structures to ensure the nature of the stationary points found (minima, no imaginary frequencies).

![Figure S1](image-url)  
**Figure S1.** Selected occupied molecular orbitals of anion 6 showing minimal N-to-Al π donation from the amido substituents. Isovalue is set at 0.05.

Xyz coordinates of optimised anions

**Anion 6**

113  
scf done: -2253.989913  

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| Al   | -0.011538 | 1.479830 | 1.242919 |
| O    | -0.029509  | -0.737596 | 1.103375 |
| N    | 1.759614   | 0.909231  | 0.325167 |
| N    | -1.772485  | 0.960770  | 0.301041 |
| C    | 1.141037   | -1.324327 | 0.670880 |
| C    | 2.121222   | -0.401302 | 0.295241 |
| C    | 3.342574   | -0.967488 | -0.099227 |
| H    | 4.150001   | -0.299044 | -0.373173 |
| C    | 3.504550   | -2.349837 | -0.214411 |
| C    | 2.437943   | -3.202069 | 0.061936 |
| H    | 2.541807   | -4.268445 | -0.072453 |
| C    | 1.218143   | -2.681729 | 0.510478 |
H  -2.702353   4.369724  -3.178386
H  -0.954798   4.190372  -3.271322
H  -1.677944   5.032371  -1.894538
C  -3.714180   0.927204   2.473391
H  -2.852410   0.279147   2.313469
C  -4.943922   0.035925   2.612802
H  -5.847063   0.624292   2.801852
H  -4.818653  -0.658557   3.448605
H  -5.102252  -0.551509   1.705972
C  -3.446895   1.714151   3.753375
H  -2.524105   2.290417   3.655756
H  -3.338777   1.034492   4.604410
H  -4.266350  -0.658557   3.448605

Anion 7
80
scf done: -2099.869794

C  3.479683   0.917155  -1.063158
C  2.755142  -0.097835  -0.401788
C  3.340367  -1.381127  -0.291006
C  4.604779  -1.613281  -0.814605
C  5.314694  -0.611600  -1.455731
C  4.743057   0.640576  -1.576180
N  1.462555   0.132920   0.109491
Si  1.317127   0.696545   1.725887
C  1.060508   2.550755   1.870815
C  2.571389  -2.511527   0.350984
C  1.825303  -3.312686  -0.712684
C  2.911482   2.306131  -1.238614
C  2.639848   2.616437  -2.706967
Al  0.000028  -0.000310  -1.173227
N  -1.462570  -0.132938   0.109519
Si  -1.317123  -0.696361   1.725974
C  -2.814694  -0.255644   2.761689
C  -2.755106   0.097834  -0.401844
C  -3.479630  -0.917174  -1.063199
C  -4.743034  -0.640641  -1.576173
C  -5.314728   0.611503  -1.455676
C  -4.604827   1.613208  -0.814570
C  -3.340370   1.381109  -0.291052
C  -2.911386  -2.306133  -1.238665
C  -2.640117  -2.616591  -2.707053
C  -2.571368   2.511547   0.350842
C  -1.825444   3.312678  -0.712964
C  3.429729  -3.426165  1.214325
C  3.807283  3.368623  -0.609456
C -3.806954  -3.368608  -0.609142
C -3.429618  3.426195  1.214258
C  2.814617  0.255899  2.761731
O  0.000027  0.000066  2.425864
C -1.060601  -2.550568  -1.871066
H  5.044660  -2.601031  -0.723631
H  6.301363  -0.809094  -1.861229
H  5.288482  -3.766968  -1.290530
H  4.137463  -4.008867  0.617174
H  2.795451  -4.137975  1.750383
H  1.950704  2.321659  -0.721693
H  1.935563  1.891134  -3.120961
H  3.561800  2.580359  -3.296323
H  2.206809  3.616069  -2.815282
H  4.769624  3.436072  -1.126015
H  4.012688  3.143449  0.440026
H  3.332344  4.352989  -0.661897
H  0.784691  2.812578  2.896865
H  0.257738  2.882534  1.208685
H  1.962779  3.107981  1.608057
H  2.943588  -0.826567  2.829720
H  2.697038  0.649251  3.775886
H  3.728499  0.675033  2.332718
H  -2.943400  0.826819  2.830214
H  -2.697634  -0.649615  3.775661
H  -3.728547  -0.674281  2.332106
H  -0.257079  -2.882236  1.209780
H  -1.962545  -3.107829  1.607283
H  -0.785865  -2.812469  2.897388
H  -5.288446  -1.429074  -2.086400
H  -6.301429  0.808951  -1.861118
H  -5.044743  2.600938  -0.723567
H  -1.950466  -2.321537  -0.721999
H  -1.935977  -1.891296  -3.121305
H  -3.562223  -2.580639  -3.296174
H  -2.207046  -3.616209  -2.815366
H  -4.769434  -3.436154  -1.125429
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | -4.012083 | -3.143335 | 0.440374 |
| H    | -3.331983 | -4.352957 | -0.661614 |
| H    | -1.821004 | 2.049452  | 0.995374  |
| H    | -2.531411 | 3.766850  | -1.415252 |
| H    | -1.155706 | 2.666964  | -1.290847 |
| H    | -1.229839 | 4.111722  | -0.259545 |
| H    | -4.002785 | 2.857095  | 1.950437  |
| H    | -4.137428 | 4.008887  | 0.617190  |
| H    | -2.795277 | 4.138017  | 1.750227  |

**Anion 8**

85

scf done: -2103.141938

**C**

-3.368196  -1.366148  -0.367426
-2.749505  -0.101248  -0.485055
-3.365195  0.873740  -1.301445
-4.563379  0.577610  -1.943115
-5.172103  -0.655920  -1.810360
-4.563661  -1.620732  -1.025918

**N**

-1.528778  0.156150  0.184066

**Al**

-0.000120  0.001008  -1.022088

**Si**

1.676692   0.867567  1.752186

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85

scf done: -2103.141938

**C**

-3.368196  -1.366148  -0.367426
-2.749505  -0.101248  -0.485055
-3.365195  0.873740  -1.301445
-4.563379  0.577610  -1.943115
-5.172103  -0.655920  -1.810360
-4.563661  -1.620732  -1.025918

**N**

-1.528778  0.156150  0.184066

**Al**

-0.000120  0.001008  -1.022088

**Si**

1.676683   0.867567  1.752186
-1.039550  2.639884  1.799549
-0.761535  -0.054013  3.117708
-0.761334  0.057126  3.117569

**Si**

1.676683   0.865219  1.752676
-3.478974  -0.889402  2.303262
-3.478942  0.892619  2.302803
 1.040532  -2.637852  1.802197
Anion 10

61

scf done: -2033.350368

H  4.205744  2.022464  2.074687
H  2.991349  0.865670  2.655529
C  3.627613  1.132173  1.806714
H  4.330316  0.313144  1.638737
Si  2.544947  1.495015  0.306224
C  1.550058  3.040720  0.756383
H  1.081933  3.489773 -0.122326
H  0.771522  2.827696  1.495883
C  2.223162  3.789258  1.187730
C  3.667540  2.101862 -1.095536
H  4.150082  3.044245 -0.814924
H  4.447370  1.381938 -1.349402
H  3.077028  2.287689 -1.997911
C  1.467623  0.061456 -0.177576
Si  2.440608 -1.518879 -0.267543
C  2.613557 -2.395049  1.391167
H  1.637427 -2.694588  1.781381
H  3.234745 -3.291149  1.286127
H  3.069757 -1.745834  2.141593
C  4.211192 -1.342308 -0.937157
H  4.206580 -0.918797 -1.945726
H  4.677544 -2.332045 -0.992635
H  4.845773 -0.709502 -0.313232
C  1.707736 -2.772659 -1.481049
H  0.742911 -3.167592 -1.162669
H  1.578607 -2.334471 -2.474580
H  2.399169 -3.616311 -1.576374
C  0.687552  0.368628 -1.475783
H  0.535589  1.450605 -1.575045
H  1.231503  0.074548 -2.388481
|    |    |    |    |
|----|----|----|----|
| C  | -0.690499 | -0.295719 | -1.481038 |
| H  | -0.538535 | -1.373226 | -1.617927 |
| H  | -1.241932 | 0.026201 | -2.380079 |
| C  | -1.464455 | -0.028756 | -0.168851 |
| Si | -2.490783 | -1.503471 | 0.306694 |
| C  | -1.456344 | -2.971954 | 0.898480 |
| H  | -2.119466 | -3.803995 | 1.158896 |
| H  | -0.878096 | -2.708856 | 1.789961 |
| H  | -0.761545 | -3.30298 | 0.137086 |
| C  | -3.488031 | -2.199413 | -1.146011 |
| H  | -4.239709 | -1.493765 | -1.504950 |
| H  | -3.997710 | -3.123216 | -0.852498 |
| H  | -2.826508 | -2.436961 | -1.984357 |
| C  | -3.690520 | -1.168292 | 1.722990 |
| H  | -4.206791 | -2.095274 | 1.993018 |
| H  | -4.448112 | -0.420656 | 1.479018 |
| H  | -3.134785 | -0.819407 | 2.597900 |
| Si | -2.496502 | 1.512032 | -0.257781 |
| C  | -4.191292 | 1.278915 | -1.085804 |
| H  | -4.700180 | 2.245812 | -1.163783 |
| H  | -4.845143 | 0.601140 | -0.532568 |
| H  | -4.077687 | 0.879366 | -2.098010 |
| C  | -1.713070 | 2.860100 | -1.326423 |
| H  | -1.467782 | 2.493834 | -2.326814 |
| H  | -0.803076 | 3.261502 | -0.879604 |
| H  | -2.424538 | 3.685049 | -1.437120 |
| C  | -2.836443 | 2.304281 | 1.417275 |
| H  | -3.354654 | 1.623551 | 2.095097 |
| H  | -3.453353 | 3.200738 | 1.291819 |
| H  | -1.901949 | 2.590570 | 1.907580 |
| Al | -0.000433 | 0.048576 | 1.372767 |

**Anion 11**

58

scf done: -1620.483194

|    |    |    |    |
|----|----|----|----|
| C  | -3.976482 | 1.769490 | 1.576770 |
| Si | -2.937965 | 1.600792 | 0.010424 |
| C  | -1.708147 | 3.033394 | 0.003924 |
| C  | -2.027837 | -0.000077 | -0.130364 |
| Si | -2.938424 | -1.600672 | 0.010539 |
| C  | -4.109455 | -1.918344 | -1.445598 |
| Al | -0.543531 | -0.000369 | 1.400062 |
| N  | 0.705286 | -0.000112 | -0.066153 |
| C  | 2.155642 | -0.000086 | -0.044344 |
C 2.734961  -1.249004  -0.732758  
C 4.261330  -1.248767  -0.687776  
C 4.791608  -0.000152  -1.391037  
C 4.261286   1.248566  -0.687776  
C 2.734915   1.248729  -0.732986  
C 4.724087  -1.245044   0.767092  
C 4.180484   0.000099   1.464196  
C 2.655137   0.000072   1.401551  
C 4.724049   1.245132   0.766870  
C 0.103592  -0.000037  -1.304211  
C -3.976449  -1.768890   1.577235  
C -1.709013  -3.033608   0.003219  
C -4.108456  1.918806  -1.446068  
H -1.700549   0.000031  -2.392681  
H  0.724284  -0.000027  -2.201145  
H -3.380646  -1.503348   2.454858  
H -4.319732  -2.802310   1.692686  
H -4.857022  -1.122506   1.557837  
H -0.982601  -2.892197  -0.801967  
H -2.209989  -3.996190  -0.142704  
H -1.157935  -3.072193   0.947515  
H -4.928432  -1.194012  -1.462879  
H -4.545444  -2.921432  -1.387266  
H -3.573539  -1.838170  -2.395570  
H -3.572513  1.837712  -2.395943  
H -4.543688  2.922249  -1.388291  
H -4.927996  1.95093  -1.463044  
H -4.857413  1.123603   1.557196  
H -4.319214  2.803120   1.692022  
H -3.381084  1.503725   2.454605  
H -1.157980  3.071931   0.948755  
H -2.208800  3.996069  -0.142521  
H -0.980993  2.891802  -0.800552  
H  2.329954  -2.133149  -0.228974  
H  2.392684  -1.289911  -1.771445  
H  2.392667  1.289438  -1.771686  
H  2.329864  2.132951  -0.229369  
H  2.245282  -0.872980   1.920396  
H  2.245258  0.873231   1.920202  
H  4.643399  -2.143833  -1.193403  
H  4.474788  -0.000246  -2.440537  
H  5.888790  -0.000136  -1.383182  
H  4.643306  2.143557  -1.193788  

S11
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| H    | 4.361388  | 2.145408  | 1.275080  |
| H    | 5.820312  | 1.260800  | 0.816837  |
| H    | 4.495778  | 0.000192  | 2.513876  |
| H    | 5.820350  | -1.260666 | 0.817067  |
| H    | 4.361452  | -2.145236 | 1.275467  |
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