Electronic Supplementary Information for Dalton Transactions


**SUPPORTING INFORMATION**

# Mixed Donor-Functionalised Phosphinomethanide Complexes of the Alkali Metals; Synthesis, Structures, and Solution Dynamics

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**Computational details:**

Geometry optimisations on the gas-phase molecules were performed with the Gaussian03 suite of programs (revision E.02)[18] on a 224-core Silicon Graphics Altix 4700 computer with 1.6 GHz Montecito Itanium2 processors and 896 Gb of memory, via the EPSRC National Service for Computational Chemistry Software (http://www.nsccs.ac.uk) or via the UK National Grid Service. Optimisations were performed using the B3LYP hybrid functional[19] with a 6-31G(d,p) all-electron basis set[20] on all atoms [default parameters were used throughout]; minima were confirmed by the absence of imaginary vibrational frequencies. NMR shielding tensors were calculated using the GIAO method[21] at the B3LYP/6-311+G(2d,p)//6-31G(d,p) level of theory;[22] chemical shifts are quoted in ppm relative to TMS calculated at the same level of theory.

18. Gaussian03, Revision E.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

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Final atomic coordinates for **12a**:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.826911 | -1.162446 | -2.553381 |
| 2 | 6 | 0 | -0.924702 | -1.448678 | -1.519876 |
| 3 | 6 | 0 | -1.977287 | -2.002720 | -3.657169 |
| 4 | 6 | 0 | -0.117797 | -2.609742 | -1.637654 |
| 5 | 6 | 0 | -1.211528 | -3.162822 | -3.752443 |
| 6 | 6 | 0 | -0.292782 | -3.453855 | -2.743809 |
| 7 | 15 | 0 | -0.688385 | -0.154956 | -0.165530 |
| 8 | 6 | 0 | -2.028006 | -2.580972 | 3.651647 |
| 9 | 6 | 0 | -1.204419 | -1.459504 | 3.762212 |
| 10 | 6 | 0 | -2.438408 | -2.994794 | 2.386796 |
| 11 | 6 | 0 | -0.786547 | -0.747820 | 2.631226 |
| 12 | 6 | 0 | -2.044696 | -2.278800 | 1.253341 |
| 13 | 6 | 0 | -1.225944 | -1.141454 | 1.340930 |
| 14 | 6 | 0 | 0.153577 | 0.420224 | 2.812619 |
| 15 | 8 | 0 | 1.540226 | 0.079917 | 2.524937 |
| 16 | 7 | 0 | 2.250254 | -2.355181 | -0.706404 |
| 17 | 6 | 0 | 0.914299 | -3.019346 | -0.599988 |
| 18 | 6 | 0 | 2.145540 | -0.720834 | 3.532529 |
| 19 | 6 | 0 | 2.845340 | -2.561148 | -2.032824 |
| 20 | 6 | 0 | 3.133022 | -2.927174 | 0.319208 |
| 21 | 6 | 0 | -1.749097 | 1.229870 | -0.381638 |
| 22 | 14 | 0 | -0.936944 | 2.723950 | -1.091332 |
| 23 | 14 | 0 | -3.518149 | 1.325462 | 0.162338 |
| 24 | 6 | 0 | -4.486696 | 2.716404 | -0.721356 |
| 25 | 6 | 0 | -3.700996 | 1.700391 | 2.028266 |
| 26 | 6 | 0 | -4.577512 | -0.232959 | -0.148684 |
| 27 | 6 | 0 | -1.033574 | 4.285676 | 0.010429 |
| 28 | 6 | 0 | -1.594704 | 3.253018 | -2.805354 |
| 29 | 6 | 0 | 0.947613 | 2.501175 | -1.398582 |
| 30 | 8 | 0 | 4.162699 | 1.126739 | 0.098628 |
| 31 | 6 | 0 | 4.798221 | 1.971770 | 1.074513 |
| 32 | 6 | 0 | 5.003250 | 0.816323 | -1.024954 |
| 33 | 6 | 0 | 5.012060 | 1.918181 | -2.078005 |
| 34 | 6 | 0 | 3.749245 | 2.683357 | 1.909650 |
| 35 | 1 | 0 | -2.408700 | -0.248097 | -2.471565 |
| 36 | 1 | 0 | -2.695911 | -1.754350 | -4.433937 |
| 37 | 1 | 0 | -1.322141 | -3.833782 | -4.599566 |
| 38 | 1 | 0 | 0.305154 | -4.360432 | -2.813474 |
| 39 | 1 | 0 | -2.341452 | -3.120333 | 4.540586 |
| 40 | 1 | 0 | -0.880539 | -1.125628 | 4.745939 |
| 41 | 1 | 0 | -3.078683 | -3.866022 | 2.277110 |
| 42 | 1 | 0 | -2.387772 | -2.607019 | 0.277909 |
| 43 | 1 | 0 | -0.093211 | 1.229980 | 2.123485 |
| 44 | 1 | 0 | 0.104369 | 0.803061 | 3.840521 |
| 45 | 1 | 0 | 0.544709 | -2.817762 | 0.408128 |
| 46 | 1 | 0 | 1.061999 | -4.111571 | -0.674355 |
| 47 | 1 | 0 | 2.138425 | -0.203940 | 4.502361 |
| 48 | 1 | 0 | 1.636676 | -1.685618 | 3.644936 |
| 49 | 1 | 0 | 3.182626 | -0.891170 | 3.231790 |
| 50 | 1 | 0 | 2.216218 | -2.110455 | -2.801403 |
| 51 | 1 | 0 | 3.835007 | -2.094718 | -2.066875 |
| 52 | 1 | 0 | 2.971046 | -3.631796 | -2.272349 |
| 53 | 1 | 0 | 2.696715 | -2.777512 | 1.311552 |
| 54 | 1 | 0 | 3.294009 | -4.010939 | 0.180696 |
| 55 | 1 | 0 | 4.110856 | -2.434163 | 0.289733 |
| 56 | 1 | 0 | -5.497305 | 2.774467 | -0.298476 |
| 57 | 1 | 0 | -4.033626 | 3.706893 | -0.613319 |
| 58 | 1 | 0 | -4.591815 | 2.514968 | -1.792926 |

| | | | | | |
|---|---|---|---|---|---|
| 59 | 1 | 0 | -3.239059 | 0.916015 | 2.637790 |
| 60 | 1 | 0 | -3.212922 | 2.648036 | 2.284625 |
| 61 | 1 | 0 | -4.753931 | 1.776871 | 2.327626 |
| 62 | 1 | 0 | -5.625272 | -0.013132 | 0.092182 |
| 63 | 1 | 0 | -4.272133 | -1.079550 | 0.471837 |
| 64 | 1 | 0 | -4.539919 | -0.554926 | -1.194513 |
| 65 | 1 | 0 | -0.580958 | 5.156273 | -0.480879 |
| 66 | 1 | 0 | -2.066763 | 4.550759 | 0.258107 |
| 67 | 1 | 0 | -0.508271 | 4.126149 | 0.960222 |
| 68 | 1 | 0 | -1.458971 | 2.448831 | -3.538076 |
| 69 | 1 | 0 | -2.661255 | 3.494677 | -2.781240 |
| 70 | 1 | 0 | -1.063982 | 4.138401 | -3.178255 |
| 71 | 1 | 0 | 1.163845 | 1.619150 | -2.014097 |
| 72 | 1 | 0 | 1.330133 | 3.378538 | -1.934845 |
| 73 | 1 | 0 | 1.515294 | 2.434152 | -0.462481 |
| 74 | 1 | 0 | 5.453776 | 1.351524 | 1.704168 |
| 75 | 1 | 0 | 5.431241 | 2.706202 | 0.562113 |
| 76 | 1 | 0 | 4.598018 | -0.105891 | -1.452478 |
| 77 | 1 | 0 | 6.019612 | 0.593848 | -0.670152 |
| 78 | 1 | 0 | 3.995852 | 2.121405 | -2.426678 |
| 79 | 1 | 0 | 5.434298 | 2.850553 | -1.691893 |
| 80 | 1 | 0 | 5.619710 | 1.608378 | -2.934743 |
| 81 | 1 | 0 | 3.157236 | 3.363153 | 1.290319 |
| 82 | 1 | 0 | 3.070944 | 1.971984 | 2.388634 |
| 83 | 1 | 0 | 4.240372 | 3.272604 | 2.690825 |
| 84 | 11 | 0 | 2.056816 | 0.036326 | 0.186786 |

Final energy for **12a**: -2384.46816760 a.u. NIMAG = 0

Final atomic coordinates for **12b**:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 14 | 0 | -3.651895 | -0.830393 | 0.238677 |
| 2 | 14 | 0 | -1.787411 | -1.413342 | -2.285038 |
| 3 | 11 | 0 | 2.085287 | -0.288708 | -0.232623 |
| 4 | 15 | 0 | -0.666597 | 0.305306 | -0.047051 |
| 5 | 7 | 0 | 1.611648 | -2.266000 | 1.246054 |
| 6 | 8 | 0 | 2.319475 | 2.058857 | -0.213911 |
| 7 | 8 | 0 | 4.443195 | -0.523717 | -0.862539 |
| 8 | 6 | 0 | -2.038255 | -0.611925 | -0.645941 |
| 9 | 6 | 0 | 0.029282 | -1.335895 | -2.898426 |
| 10 | 1 | 0 | 0.385934 | -0.303510 | -2.993498 |
| 11 | 1 | 0 | 0.105464 | -1.809082 | -3.885107 |
| 12 | 1 | 0 | 0.705983 | -1.876100 | -2.225562 |
| 13 | 6 | 0 | -2.213993 | -3.278575 | -2.321989 |
| 14 | 1 | 0 | -1.573285 | -3.845852 | -1.635745 |
| 15 | 1 | 0 | -2.080557 | -3.698088 | -3.327043 |
| 16 | 1 | 0 | -3.250131 | -3.471948 | -2.024567 |
| 17 | 6 | 0 | -2.777773 | -0.629296 | -3.718745 |
| 18 | 1 | 0 | -3.856190 | -0.666938 | -3.536523 |
| 19 | 1 | 0 | -2.584278 | -1.141291 | -4.669996 |
| 20 | 1 | 0 | -2.505191 | 0.425085 | -3.845261 |
| 21 | 6 | 0 | -4.202244 | 0.635119 | 1.331614 |
| 22 | 1 | 0 | -3.551571 | 0.781704 | 2.197980 |
| 23 | 1 | 0 | -5.213849 | 0.442236 | 1.710264 |
| 24 | 1 | 0 | -4.232298 | 1.578048 | 0.775878 |
| 25 | 6 | 0 | -3.669853 | -2.356529 | 1.391484 |
| 26 | 1 | 0 | -3.428114 | -3.270850 | 0.837141 |

| | | | | | |
|---|---|---|---|---|---|
| 27 | 1 | 0 | -4.652293 | -2.500433 | 1.858694 |
| 28 | 1 | 0 | -2.934493 | -2.254649 | 2.197661 |
| 29 | 6 | 0 | -5.116965 | -1.100300 | -0.959825 |
| 30 | 1 | 0 | -5.298481 | -0.214021 | -1.578010 |
| 31 | 1 | 0 | -6.030904 | -1.293227 | -0.384618 |
| 32 | 1 | 0 | -4.974875 | -1.949337 | -1.635955 |
| 33 | 6 | 0 | -0.613537 | 0.232765 | 1.829136 |
| 34 | 6 | 0 | -0.962774 | 1.328572 | 2.639212 |
| 35 | 1 | 0 | -1.322416 | 2.237296 | 2.168060 |
| 36 | 6 | 0 | -0.887027 | 1.277899 | 4.032091 |
| 37 | 1 | 0 | -1.172303 | 2.146869 | 4.619199 |
| 38 | 6 | 0 | -0.476938 | 0.105847 | 4.662898 |
| 39 | 1 | 0 | -0.433179 | 0.043614 | 5.746283 |
| 40 | 6 | 0 | -0.137941 | -0.997960 | 3.880646 |
| 41 | 1 | 0 | 0.158700 | -1.925370 | 4.365676 |
| 42 | 6 | 0 | -0.177754 | -0.953444 | 2.480313 |
| 43 | 6 | 0 | 0.194116 | -2.207652 | 1.712068 |
| 44 | 1 | 0 | -0.007286 | -3.088423 | 2.346579 |
| 45 | 1 | 0 | -0.443735 | -2.285659 | 0.827279 |
| 46 | 6 | 0 | 1.775277 | -3.453231 | 0.393625 |
| 47 | 1 | 0 | 2.804728 | -3.505394 | 0.023690 |
| 48 | 1 | 0 | 1.094592 | -3.395379 | -0.459786 |
| 49 | 1 | 0 | 1.561607 | -4.389539 | 0.937875 |
| 50 | 6 | 0 | 2.541470 | -2.355296 | 2.378831 |
| 51 | 1 | 0 | 2.446969 | -1.472748 | 3.014735 |
| 52 | 1 | 0 | 3.568921 | -2.414446 | 2.005700 |
| 53 | 1 | 0 | 2.353717 | -3.248602 | 3.000591 |
| 54 | 6 | 0 | -0.907506 | 2.162502 | -0.342751 |
| 55 | 6 | 0 | -2.057441 | 2.565680 | -1.033486 |
| 56 | 1 | 0 | -2.791510 | 1.801456 | -1.273692 |
| 57 | 6 | 0 | -2.262931 | 3.891057 | -1.421705 |
| 58 | 1 | 0 | -3.175486 | 4.165218 | -1.944676 |
| 59 | 6 | 0 | -1.300704 | 4.857113 | -1.136432 |
| 60 | 1 | 0 | -1.446998 | 5.892220 | -1.431238 |
| 61 | 6 | 0 | -0.134035 | 4.472972 | -0.474468 |
| 62 | 1 | 0 | 0.627675 | 5.218892 | -0.254251 |
| 63 | 6 | 0 | 0.083332 | 3.144998 | -0.083616 |
| 64 | 6 | 0 | 1.391112 | 2.817966 | 0.601676 |
| 65 | 1 | 0 | 1.892791 | 3.745132 | 0.912403 |
| 66 | 1 | 0 | 1.238151 | 2.200159 | 1.488512 |
| 67 | 6 | 0 | 2.810841 | 2.777444 | -1.340096 |
| 68 | 1 | 0 | 2.002572 | 3.057766 | -2.024335 |
| 69 | 1 | 0 | 3.513221 | 2.116995 | -1.854187 |
| 70 | 1 | 0 | 3.339381 | 3.687782 | -1.023307 |
| 71 | 6 | 0 | 3.782878 | -1.708917 | -2.866047 |
| 72 | 1 | 0 | 3.386070 | -2.554845 | -2.297118 |
| 73 | 1 | 0 | 4.149893 | -2.092308 | -3.822944 |
| 74 | 1 | 0 | 2.962556 | -1.017789 | -3.079893 |
| 75 | 6 | 0 | 4.913623 | -1.029102 | -2.119462 |
| 76 | 1 | 0 | 5.734743 | -1.737785 | -1.935505 |
| 77 | 1 | 0 | 5.325084 | -0.197009 | -2.711120 |
| 78 | 6 | 0 | 5.506510 | 0.082759 | -0.113082 |
| 79 | 1 | 0 | 5.914909 | 0.926414 | -0.690026 |
| 80 | 1 | 0 | 6.316009 | -0.651720 | 0.012249 |
| 81 | 6 | 0 | 5.000369 | 0.557634 | 1.236211 |
| 82 | 1 | 0 | 4.205497 | 1.297928 | 1.113246 |
| 83 | 1 | 0 | 5.821354 | 1.021887 | 1.791538 |
| 84 | 1 | 0 | 4.624248 | -0.278213 | 1.833221 |

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Final energy for **12b**: -238.47081009 a.u. NIMAG = 0