Supplementary Material (ESI) for Dalton Transactions

Hydrogen Fluoride Adduct of an Ambiphilic Phosphine-Borane: NMR Characterization and Theoretical Analysis of the Bonding Situation

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SUPPLEMENTARY INFORMATION

Contents

Computational details

Phosphorus and fluorine were treated with a Stuttgart–Dresden pseudopotential in combination with its adapted basis set.[1] The basis set has been augmented by a set of polarization function (d for P and F). Carbon, boron and hydrogen atoms have been described with a 6–31G(d,p) double–ζ basis set.[2] Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91.[3,4] Geometry optimisations were carried out without any symmetry restrictions, the nature of the *extrema* (*minimum*) was verified with analytical frequency calculations. The electronic structure of the 1:1 adduct **3** was studied using Natural Bond Orbital (NBO) analysis (NBO-3.1 program).[5,6] All these computations have been performed with the Gaussian 03[7] suite of programs.

[1] A. Bergner, M. Dolg, W. Kuechle, H. Stoll and H. Preuss, *Mol. Phys.,* 1993, **80**, 1431.
[2] W. J. Hehre, R., Ditchfield, J. A. Pople, *J. Chem. Phys.,* 1972, **56**, 2257.
[3] J. P. Perdew and Y. Wang, *Phys. Rev. B,* 1992, **45**, 13244.
[4] Becke, A. D., *J. Chem. Phys.,* 1993, **98**, 5648.
[5] NBO version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold.
[6] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.
[7] Gaussian 03 (Revision D.02), M. J., Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P., Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, 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, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2006.

Compound [*o*–*i*Pr$_2$P(C$_6$H$_4$)BMes$_2$] 1

72
E= -1198.3356642 a.u.
G= -1197.782195 a.u.

C 3.9643100074 8.7827557169 -1.5945365532	C 1.4259300956 4.2240104476 2.3726889312
C 3.2460412408 8.3609791639 -0.4460981465	C 1.8162865677 4.2727115249 1.0345827117
C 1.884739809 8.7080370223 -0.3506110633	H 1.5195584439 3.4667886576 0.3651883109
H 1.3129092413 8.352790767 0.5038161857	C 2.5753446049 5.327171254 0.5237220712
C 1.2514991167 9.4909949686 -1.3128507839	C 3.0479156874 7.3635531166 3.7514286715
H 0.2023334196 9.7521581524 -1.2015415713	H 2.7788341957 8.374918863 3.4313868757
C 1.9686981727 9.9132422096 -2.4280427357	H 4.128606616 7.3622386876 3.919738449
H 1.4882043815 10.5121447963 -3.1976230147	H 2.5562859059 7.184053029 4.7119130178
C 3.3066645011 9.5433292912 -2.5698043465	C 0.5624787709 3.1059149433 2.8917758917
H 3.834746384 9.8478513923 -3.4689066423	H 0.7398070021 2.9224152827 3.9557608711
P 5.7248895317 8.1663239718 -1.8106891658	H 0.7455329797 2.1731547877 2.3497085816
C 5.8317367234 7.9506917661 -3.6981216303	H -0.5021383678 3.3450786504 2.7756748361
H 5.5641533529 8.8912425448 -4.1950347899	C 2.9393294389 5.2799231689 -0.9413162449
C 4.8563039293 6.8580951684 -4.1420338403	H 2.7866629068 4.2737962918 -1.3431259586
H 4.9201266625 6.708674523 -5.2269272961	H 3.9828945532 5.5559770888 -1.1191238424
H 3.8197749469 7.1058494791 -3.8978257298	H 2.3225198029 5.9696303162 -1.526880683
H 5.0954046719 5.9018214945 -3.6628584045	C 5.1536915368 8.1085303364 1.5224251791
C 7.2624691195 7.5824242066 -4.0997960701	C 5.2625835399 9.4554224808 1.9586142298
H 7.6112563881 6.6965426329 -3.5566548103	C 6.3886835085 9.8709006665 2.6749266389
H 7.9706703683 8.3928696213 -3.9084496873	H 6.4414300586 10.903469531 3.0164900295
H 7.3076204682 7.3530562883 -5.1715658941	C 7.4433760312 9.0060509686 2.9669012454
C 6.7193394212 9.760373751 -1.4525034189	C 7.3446804989 7.689401357 2.515373349
H 6.2492042022 10.0982516988 -0.5214494525	H 8.1602305652 6.9967172815 2.7170313476
C 8.1761002478 9.4229674991 -1.1190906942	C 6.2269815742 7.2264341413 1.8173170075
H 8.7283377986 9.0587926894 -1.9914017607	C 4.1819435692 10.4824799275 1.7063353444
H 8.2377851276 8.6612063306 -0.3372344418	H 4.4017524326 11.4096349371 2.243450552
H 8.6957091979 10.318601737 -0.7568150532	H 3.1933935189 10.1418379998 2.0308651355
C 6.6077852992 10.8800780942 -2.4837882034	H 4.0911620028 10.7248001929 0.6428759013
H 7.137486254 11.7738283341 -2.129986121	C 8.6326578294 9.4675372905 3.7658392915
H 5.5677782256 11.1669591286 -2.6636428131	H 8.7933668182 10.5446754284 3.6609671912
H 7.0563069905 10.6010330475 -3.4437256284	H 9.5479932724 8.9547964666 3.4546800673
B 3.850904986 7.5874630903 0.7966982477	H 8.4933489019 9.261291704 4.8345587085
C 3.0098605977 6.3769743592 1.375502373	C 6.2329393816 5.7985367032 1.3342678968
C 2.6381153015 6.3137119941 2.7447509415	H 6.3016243292 5.768415703 0.2397555879
C 1.84729781 5.2584447936 3.2075139518	H 5.3216907725 5.2661970807 1.6193379025
H 1.5605157036 5.240304892 4.2577063067	H 7.0891410539 5.2514670765 1.7392866603

1:1 adduct [*o*–*i*$Pr_2P(C_6H_4)BMes_2$•HF] 3

74
E= -1223.272232 a.u.
G= -1222.701193 a.u.

C	2.248666	-1.372083	0.407415	H	0.533064	-6.288207	-3.657225
C	1.117501	-1.029898	-0.379905	H	0.104334	-3.225461	-0.170076
C	0.015731	-0.454939	0.319282	H	1.205098	-4.465876	1.557410
C	0.054177	-0.274319	1.706140	H	1.131251	-5.995132	0.670668
C	1.155903	-0.643437	2.475400	H	2.181245	-4.676025	0.111988
C	2.244991	-1.182031	1.797267	H	-1.439311	-4.438211	1.304733
B	0.903884	-1.297506	-2.002656	H	-2.141653	-4.333822	-0.309135
C	1.937551	-2.371114	-2.711184	H	-1.428125	-5.861131	0.262321
C	3.082787	-1.903360	-3.381950	H	-1.403734	-7.763684	-3.199182
C	4.002913	-2.742691	-3.998472	H	-1.856447	-6.789430	-1.799708
C	3.806974	-4.123415	-3.986322	H	-1.918523	-6.089461	-3.425302
C	2.666744	-4.635409	-3.382082	H	0.947421	-8.304200	-2.342742
C	1.739451	-3.773411	-2.766063	H	1.957199	-7.028097	-1.651437
P	0.228134	-4.547994	-2.078371	H	0.461641	-7.515473	-0.843338
C	0.047132	-4.317907	-0.238935	H	-0.805993	0.180602	2.196992
C	-1.321924	-4.771280	0.268360	H	3.135503	-1.453222	2.363577
C	-1.244028	0.011009	-0.377896	H	-0.643747	0.977647	-5.943921
C	1.164649	-0.466147	3.971155	H	1.825524	3.286082	-3.335760
C	3.541828	-1.908830	-0.167306	H	-0.934191	-1.195309	-5.706047
C	0.792735	0.035337	-2.971146	H	0.009298	-2.170020	-4.570413
C	1.444244	1.268414	-2.705282	H	-1.541318	-1.507197	-4.070217
C	1.310387	2.357021	-3.577873	H	1.733322	1.566400	-0.569736
C	0.547065	2.293316	-4.739244	H	3.052295	0.711162	-1.341290
C	-0.064121	1.075245	-5.026237	H	2.867679	2.446065	-1.602378
C	0.050733	-0.034832	-4.183071	H	1.238486	4.165578	-5.571510
C	2.317424	1.505939	-1.492614	H	0.270348	3.189240	-6.688186
C	-0.641927	-1.294921	-4.655525	H	-0.511845	4.068166	-5.374394
C	0.381296	3.488191	-5.640644	H	2.182182	-0.499782	4.372374
C	0.116940	-6.335442	-2.643017	H	0.718873	0.490626	4.263378
C	-1.352467	-6.757422	-2.769545	H	0.588523	-1.253841	4.473772
C	0.923839	-7.342360	-1.819269	H	3.421256	-2.865808	-0.681952
C	1.211106	-4.910606	0.557917	H	3.981625	-1.225230	-0.900526
H	-0.925248	-4.011837	-2.683168	H	4.279800	-2.050701	0.628437
H	2.509143	-5.708519	-3.406157	H	-1.779377	0.732483	0.247989
H	4.518699	-4.793492	-4.459673	H	-1.027022	0.481353	-1.339283
H	4.873034	-2.321630	-4.496083	H	-1.921467	-0.823005	-0.586264
H	3.238576	-0.828502	-3.421985	F	-0.389948	-2.022993	-2.042017

Compound [*p*–*i*Pr$_2$P(C$_6$H$_4$)BMes$_2$] 7

72
E= -1198.339006 a.u.
G= -1197.786440 a.u.

C	-0.709837	-1.140625	0.184387	H	-4.604999	-2.368584	-0.117501
C	0.054078	-0.049530	-0.269404	H	-0.201138	-1.976888	0.659030
C	-0.654978	1.000909	-0.886584	H	-4.796860	2.993417	1.402018
C	-2.033428	0.956219	-1.050003	H	-4.998326	1.350008	2.009856
C	-2.790827	-0.124411	-0.559897	H	-3.481289	1.822534	1.233361
C	-2.095908	-1.174793	0.059598	H	-6.954495	2.718826	-0.005083
B	1.610712	-0.010282	-0.099135	H	-7.071321	1.402628	-1.184327
P	-4.614467	-0.136879	-0.919247	H	-7.145823	1.057498	0.551927
C	-5.266984	-1.543522	0.181272	H	-5.411597	-2.339872	2.192769
C	-6.678996	-1.938015	-0.269869	H	-4.197321	-1.060133	2.031844
C	2.341485	1.393989	-0.087587	H	-5.920977	-0.658638	2.060927
C	3.391134	1.691247	-0.996425	H	-6.992503	-2.860779	0.232918
C	4.000623	2.946983	-0.979555	H	-7.415362	-1.166962	-0.022784
C	3.629277	3.939095	-0.070602	H	-6.724631	-2.108311	-1.349750
C	2.613755	3.638465	0.834841	H	2.321201	4.386049	1.570837
C	1.959624	2.402660	0.832650	H	4.797823	3.152829	-1.692151
C	3.859409	0.694573	-2.028995	H	4.754710	1.057932	-2.541372
C	0.871268	2.198839	1.863838	H	4.091820	-0.275262	-1.581855
C	4.295916	5.288680	-0.079917	H	3.096002	0.521101	-2.796961
C	2.387578	-1.380930	0.058367	H	0.776630	1.158730	2.183290
C	3.199860	-1.645274	1.191862	H	1.068202	2.805553	2.753300
C	3.844325	-2.876690	1.321971	H	-0.108106	2.497486	1.473098
C	3.743926	-3.871982	0.348078	H	4.172786	5.803860	0.877217
C	2.957981	-3.604742	-0.771125	H	5.367897	5.204815	-0.285398
C	2.274142	-2.394993	-0.925552	H	3.868067	5.934483	-0.856913
C	3.361302	-0.640537	2.306950	H	4.449520	-3.060775	2.208357
C	4.488001	-5.173012	0.489645	H	2.872815	-4.359640	-1.551561
C	1.446894	-2.222751	-2.180469	H	1.873298	-2.803876	-3.004250
C	-5.139181	1.540295	-0.162720	H	0.418277	-2.570452	-2.031682
C	-6.662850	1.681397	-0.207415	H	1.380543	-1.182089	-2.505550
C	-4.567550	1.939580	1.197184	H	2.421612	-0.486759	2.850810
C	-5.186633	-1.385409	1.699605	H	4.102496	-0.983025	3.034623
H	-2.630788	-2.035882	0.448077	H	3.678588	0.335777	1.931119
H	-2.530702	1.773562	-1.567671	H	4.475204	-5.531163	1.524077
H	-0.103771	1.861872	-1.258354	H	4.056786	-5.952769	-0.144856
H	-4.731619	2.232968	-0.912582	H	5.540350	-5.059761	0.200737

1:1 adduct [*p*–*i*$Pr_2P(C_6H_4)BMes_2$•HF] 8

74
E= -1223.246987 a.u.
G= -1222.682156 a.u.

C	-1.577675	-0.535515	4.048704	H	-6.387881	-5.706823	-4.587531
C	-1.911714	-1.268146	2.874420	H	-6.418354	-4.066093	-5.235991
C	-2.512174	-2.534053	3.077814	H	-5.087944	-5.166953	-5.647428
C	-2.743114	-3.028845	4.369671	H	-1.367582	-3.746447	-6.326136
C	-2.403637	-2.312487	5.511990	H	-1.544375	-4.225726	-4.639836
C	-1.816122	-1.063145	5.321620	H	-2.703455	-4.796380	-5.855081
B	-1.631261	-0.506062	1.430802	H	-3.008985	-2.149079	-7.420532
C	-0.040135	-0.197649	1.057056	H	-4.423546	-3.073441	-6.913096
C	1.028931	-1.065344	1.404287	H	-4.274300	-1.359470	-6.477407
C	2.345649	-0.782795	1.014846	C	-2.935479	-3.449230	1.949199
C	2.675597	0.348655	0.274794	H	-3.202568	-4.010995	4.481309
C	1.627753	1.187840	-0.096977	C	-2.677950	-2.848917	6.892674
C	0.299875	0.934405	0.265774	H	-1.532251	-0.473159	6.193063
C	-2.264290	-1.198284	0.072705	C	-0.957747	0.841955	3.996588
C	-3.546487	-0.809658	-0.367357	H	-0.567656	1.126300	4.979616
C	-4.097625	-1.270765	-1.554619	H	-0.140424	0.894003	3.272899
C	-3.356803	-2.153963	-2.361588	H	-1.693815	1.589423	3.687218
C	-2.065940	-2.550481	-1.963796	H	-2.102518	-3.718422	1.290199
C	-1.543809	-2.065096	-0.774589	H	-3.346450	-4.381551	2.351161
P	-4.101432	-2.773203	-3.858502	H	-3.703649	-2.996151	1.314831
C	-4.988758	-4.397553	-3.603367	H	-2.825638	-3.933633	6.879230
C	-4.075083	-5.478004	-3.021327	H	-1.853082	-2.630393	7.579757
C	-2.952595	-2.685856	-5.334699	H	-3.582281	-2.401947	7.325871
C	-2.100061	-3.941548	-5.536451	C	0.836606	-2.331494	2.210740
C	-3.720933	-2.294783	-6.601680	H	3.136903	-1.473690	1.306157
C	-5.759590	-4.848148	-4.845220	C	4.102215	0.660772	-0.094890
H	-1.468406	-3.214898	-2.583921	H	1.846083	2.070360	-0.698682
H	-5.087195	-0.937416	-1.863750	C	-0.728733	1.919443	-0.245048
H	-4.102906	-0.106534	0.245689	H	-0.268570	2.611369	-0.959252
F	-2.372510	0.738377	1.549532	H	-1.562078	1.417303	-0.745594
H	-5.152406	-1.873657	-4.171583	H	-1.171910	2.500883	0.566778
H	-5.706863	-4.103142	-2.824874	H	0.015923	-2.950574	1.837461
H	-2.296574	-1.855684	-5.044223	H	1.748614	-2.938109	2.189220
H	-0.529130	-2.340264	-0.498210	H	0.599834	-2.115845	3.256718
H	-4.687723	-6.324461	-2.695466	H	4.702936	-0.250304	-0.186661
H	-3.361958	-5.853363	-3.760025	H	4.162281	1.202162	-1.045163
H	-3.520897	-5.116129	-2.150974	H	4.584697	1.289826	0.664543

^{1}H NMR spectrum of 2 (300 MHz, $CDCl_3$)