Electronic Supplementary Information for Dalton Transactions

Supporting Information for:

Selective halogenation at the pnictogen atom in Lewis-acid/base-stabilised phosphanylboranes and arsanylboranes

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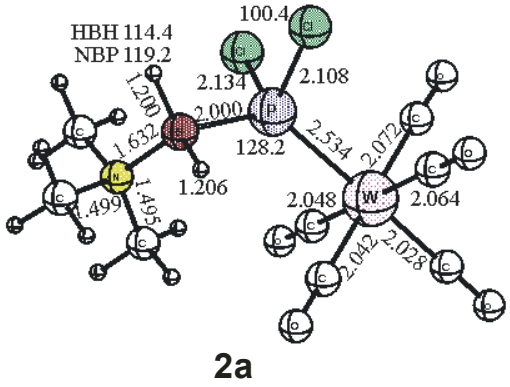
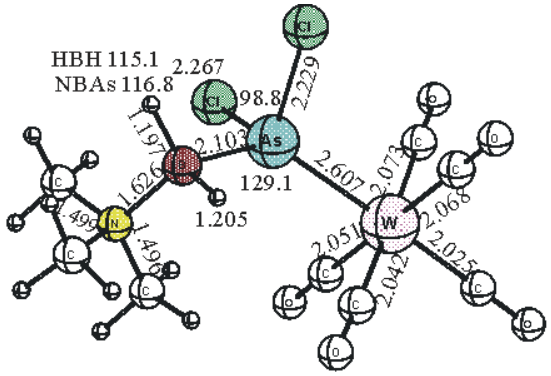
S1. Optimized structures (XYZ coordinates) of the compounds 2a and 3a and their relative energies

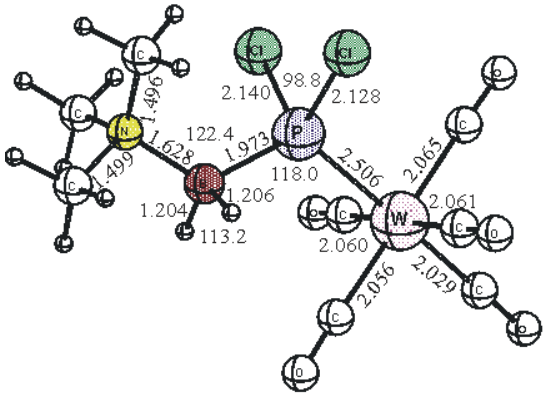
Optimized Structures of the isomers. B3LYP/6-31G*(LANL2DZ on W) level of theory.

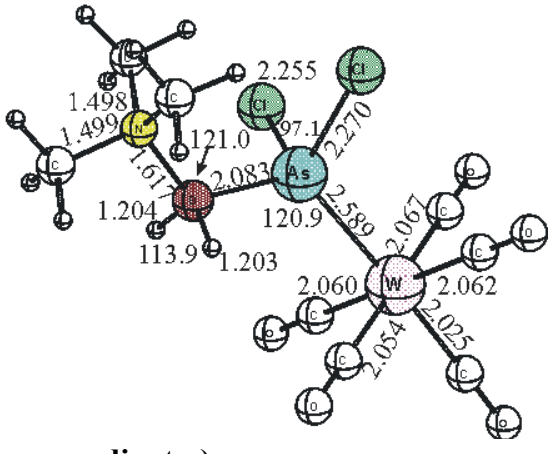


2a



3a





Optimized structures (xyz coordinates)

***cis*-W(CO)$_5$PCl$_2$BH$_2$NMe$_3$** ***trans*-W(CO)$_5$PCl$_2$BH$_2$NMe$_3$**

W	–1.203124	–0.258042	0.007601
C	–2.971587	–1.240877	0.146168
C	–0.463879	–1.774157	–1.144045
C	–1.951290	1.305931	1.141834
C	–1.871227	0.682970	–1.709496
C	–0.546782	–1.191993	1.708070
O	–0.161166	–1.732420	2.656364
O	–2.258655	1.190748	–2.667503
O	–2.379126	2.172075	1.767870
O	–0.044103	–2.637439	–1.793601
O	–3.978607	–1.803577	0.230066
B	2.722666	0.314996	–0.961276
N	3.588734	–0.830002	–0.183791
H	3.449763	1.259421	–1.097686
H	2.335298	–0.169537	–1.995618
C	4.319263	–0.268565	0.997443
C	4.605453	–1.307733	–1.176865
C	2.776479	–2.005068	0.256664
H	4.951076	–1.045998	1.439079
H	3.599001	0.089241	1.731684
H	4.932921	0.568631	0.663419
H	5.269885	–2.034089	–0.697684
H	5.180396	–0.451584	–1.531918
H	4.088974	–1.769410	–2.018716
H	3.438455	–2.780892	0.654548
H	2.220726	–2.394477	–0.596087
H	2.080989	–1.695264	1.036440
P	1.012412	0.960886	–0.150647
Cl	1.538911	1.797039	1.740221
Cl	0.858601	2.710179	–1.308547

W	–0.639234	0.948888	–3.117632
C	–0.514351	1.990419	–4.854904
C	–0.546259	2.721041	–2.079916
C	–0.733323	–0.834274	–4.154896
C	–2.694235	1.099198	–3.177781
C	1.414621	0.810800	–3.050561
O	2.566021	0.745232	–3.015652
O	–3.842867	1.195158	–3.216362
O	–0.785288	–1.826381	–4.739167
O	–0.490955	3.728762	–1.518366
O	–0.443224	2.580649	–5.847000
B	–0.831441	0.717631	0.720560
N	–0.670696	0.014941	2.180218
H	–1.918658	1.236388	0.674147
H	0.074830	1.502655	0.609028
C	–1.519108	–1.205894	2.349795
C	–1.108191	1.040037	3.182579
C	0.758111	–0.336177	2.465547
H	–1.461927	–1.546062	3.388901
H	–1.160014	–1.990592	1.684714
H	–2.549435	–0.961276	2.090630
H	–0.935159	0.659247	4.194424
H	–2.168153	1.249402	3.036913
H	–0.536059	1.955378	3.024617
H	0.834485	–0.763271	3.470668
H	1.360660	0.570397	2.398418
H	1.105099	–1.056250	1.725935
P	–0.795379	–0.315749	–0.959718
Cl	0.724498	–1.810485	–0.771835
Cl	–2.504451	–1.581791	–0.89673

***cis*–W(CO)$_5$AsCl$_2$BH$_2$NMe$_3$**

W	2.416354	–1.266670	–1.075437
C	4.420372	–1.471170	–1.277365
C	2.695855	0.127994	0.389142
C	2.064052	–2.668060	–2.561655
C	2.419100	0.233671	–2.498251
C	2.386413	–2.747685	0.342889
O	2.358257	–3.562578	1.162962
O	2.434691	1.073326	–3.286083
O	1.869402	–3.444958	–3.387936
O	2.835897	0.907608	1.235569
O	5.565181	–1.590195	–1.389695
B	–1.200243	0.251824	0.581039
N	–1.338168	–0.287819	2.108633
H	–2.303821	0.435080	0.155194
H	–0.489803	1.225391	0.593611
C	–2.458309	–1.276391	2.233269
C	–1.670062	0.910794	2.945335
C	–0.080714	–0.902608	2.637376

trans–W(CO)$_5$AsCl$_2$BH$_2$NMe$_3$

W	–1.517617	0.186308	–0.010930
C	–3.478466	0.686369	–0.080317
C	–1.037364	2.173281	0.184903
C	–1.974873	–1.821654	–0.188297
C	–1.618740	0.017253	2.041848
C	–1.400690	0.349080	–2.061355
O	–1.341917	0.446624	–3.209378
O	–1.682194	–0.069371	3.189601
O	–2.235449	–2.939583	–0.282137
O	–0.781454	3.293924	0.301418
O	–4.598327	0.971852	–0.123377
B	2.433428	1.090171	–0.405885
N	4.000471	0.835654	–0.101704
H	2.077174	2.032614	0.251412
H	2.288615	1.240856	–1.591729
C	4.297491	0.940192	1.364123
C	4.747398	1.924062	–0.812335
C	4.484898	–0.487267	–0.609484

H	–2.545148	–1.599663	3.275587	H	5.371278	0.805800	1.528495
H	–2.253593	–2.131085	1.589343	H	3.738082	0.171730	1.896483
H	–3.382848	–0.796417	1.911163	H	3.987066	1.925638	1.713873
H	–1.877089	0.593473	3.972570	H	5.815015	1.844081	–0.583828
H	–2.547162	1.402240	2.521785	H	4.365378	2.890110	–0.478801
H	–0.826055	1.600808	2.927783	H	4.584923	1.823414	–1.885738
H	–0.195109	–1.113018	3.705484	H	5.571758	–0.544788	–0.492979
H	0.747313	–0.209260	2.485562	H	4.212326	–0.584474	–1.660632
H	0.115785	–1.837401	2.110272	H	4.009540	–1.286575	–0.041967
As	–0.156270	–0.978064	–0.768561	As	1.010162	–0.375110	–0.000179
Cl	–1.171240	–3.001843	–0.659391	Cl	1.482313	–2.020588	–1.468063
Cl	–1.128853	–0.209364	–2.621265	Cl	1.680835	–1.470145	1.871474

Relative Energies of the isomers. B3LYP/6-31G*(LANL2DZ on W) level of theory.

Compound	Relative energy, kJ mol^{-1}
cis–$W(CO)_5PCl_2BH_2NMe_3$	6.8
trans–$W(CO)_5PCl_2BH_2NMe_3$	0
cis–$W(CO)_5AsCl_2BH_2NMe_3$	6.0
trans–$W(CO)_5AsCl_2BH_2NMe_3$	0

In both cases *trans* isomer is more stable, but the difference between the isomers is only ~7 kJ mol^{-1}.