Electronic Supplementary Information for Dalton Transactions

Synthesis, Photoelectron Spectroscopy and Quantum Chemical Study of Kinetically Unstabilized Phosphines Complexed by Borane

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Supporting Information (17 pages)

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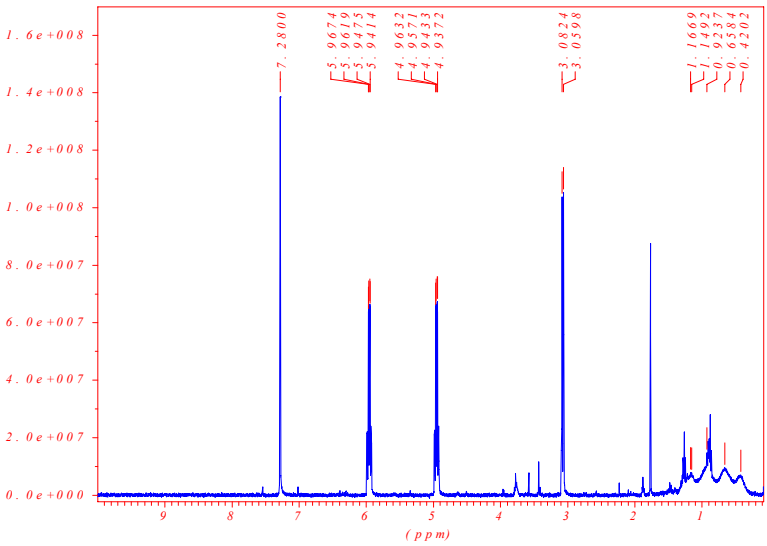
Preparation of Diborane[S1]

Orthophosphoric acid (30 mL of 85 % aqueous solution) was introduced into a 500 mL two-necked flask equipped with a stirring bar and a cell containing the potassium borohydride (1.6 g, 29 mmol). The flask was fitted on the vacuum line and degassed for 30 min. The potassium borohydride was slowly added by portions in about 1 hr. During and after addition, the formed diborane was distilled off *in vacuo* from the reaction mixture. A cold trap (-80 ^{o}C) selectively removed less volatile products and the diborane was condensed in a second cold trap (-196 ^{o}C). At the end of the reaction, this second cell was disconnected from the vacuum line by stopcocks and kept at 77 K in a liquid nitrogen bath. Yield: 0.25 g, 8.7 mmol of B_2H_6 (60 %).

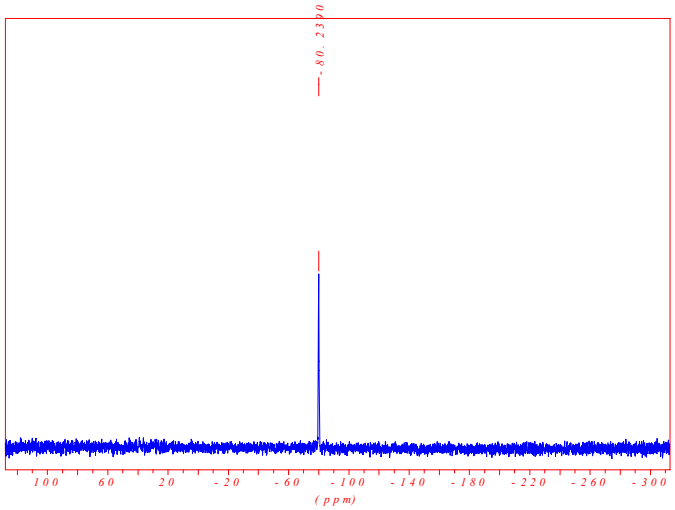
S1. A. D. Norman, W. L. Jolly *Inorganic Syntheses*, 1968, **11**, 15-19.

Flash vacuum pyrolysis of phosphine-boranes (7) and (8). Phosphine-borane **7**, **8** (1 mmol) was vaporized in a vacuum line equipped with a short oven (15 cm) heated to 300 °C and a cold finger (77 K). The gaseous flow was condensed on the cold finger and an NMR solvent ($CDCl_3$, 600 µL) was added at this step. The analysis was performed by ^{1}H and ^{31}P NMR spectroscopy. Only the free phosphine **1**, **2** was observed in a 97 and 93% yield respectively. BH_3, the second product of the thermolysis and the second component of the gaseous flow, was not condensed at 77 K in vacuo (10^{-1} mbar).

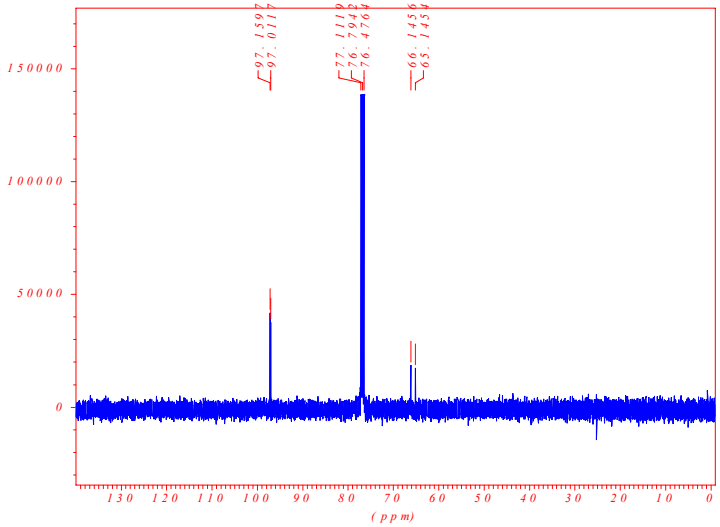
$HC{\equiv}CPH_2\text{-}BH_3$ (10) ^{1}H NMR ($CDCl_3$, 293K)



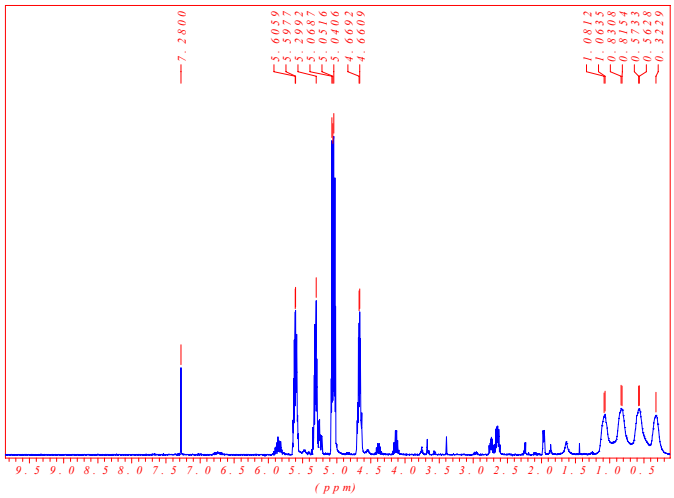
$HC{\equiv}CPH_2\text{-}BH_3$ (10) ^{31}P NMR ($CDCl_3$, 293K)



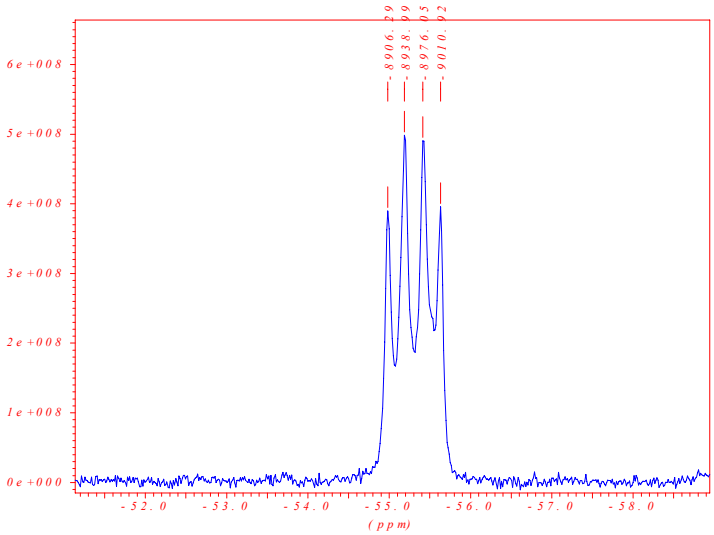
$HC{\equiv}CPH_2\text{-}BH_3$ (10) ^{13}C NMR ($CDCl_3$, 293K)



CH_2=C=CHPH_2-BH_3 (12) ^{1}H NMR ($CDCl_3$, 293K)



CH_2=C=CHPH_2-BH_3 (12) ^{31}P NMR ($CDCl_3$, 293K)



CH_2=C=CHPH_2-BH_3 (12) ^{13}C NMR ($CDCl_3$, 293K)

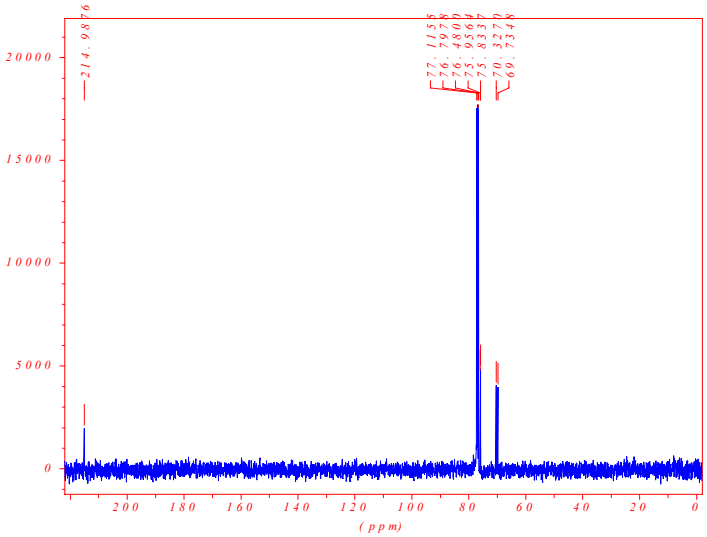


Table S1. NPA Charges of Heavy Atoms in the Investigated Structures[a]

	P	C(1)	C(2)	C(3)	B
1	0.296	-0.870			
2I	0.297	-0.470	-0.347		
2II	0.318	-0.472	-0.373		
3I	0.311	-0.681	-0.176	-0.389	
3II	0.303	-0.675	-0.182	-0.382	
3III	0.310	-0.674	-0.182	-0.378	
3IV	0.305	-0.697	-0.175	-0.388	
3V	0.291	-0.687	-0.172	-0.391	
4	0.357	-0.372	-0.195		
5I	0.320	-0.721	-0.022	-0.238	
5II	0.331	-0.716	-0.024	-0.233	
6I	0.329	-0.567	0.104	-0.475	
6II	0.334	-0.565	0.087	-0.475	
7	0.846	-0.893			-0.658
8I	0.821	-0.514	-0.295		-0.663
8II	0.819	-0.496	-0.316		-0.643
9I	0.829	-0.701	-0.189	-0.368	-0.638
9II	0.827	-0.696	-0.190	-0.369	-0.643
9III	0.849	-0.698	-0.193	-0.348	-0.659
9IV	0.835	-0.718	-0.169	-0.381	-0.649
9V	0.833	-0.709	-0.179	-0.372	-0.649
10	0.834	-0.393	-0.115		-0.620
11I	0.859	-0.741	-0.034	-0.209	-0.660
11II	0.857	-0.734	-0.037	-0.198	-0.657
12I	0.844	-0.608	0.139	-0.448	-0.653
12II	0.848	-0.593	0.120	-0.461	-0.648

[a] B3LYP/aug-cc-pVDZ level, the numbers of the carbon atoms are in order of the distance from phosphorus atom

Table S2. Calculated Wiberg Indices (B3LYP/aug-cc-pVTZ level)

	Wiberg index
7	0.968
8I	0.967
8II	0.956
9I	0.955
9II	0.959
9III	0.968
9IV	0.965
9V	0.964
10	0.934
11I	0.967
11II	0.968
12I	0.966
12II	0.958

Table S3. Calculated P-C Rotational Barriers (at B3LYP/aug-cc-pVTZ level)

		ΔE(+ZPE)	ΔG
1	**TS1**	6.34	7.37
2	**TS1**	4.17	6.09
	TS2	10.68	12.60
3	**TSI1**	10.77	12.10
	TSI2	10.42	11.67
	TSI3	7.47	8.94
	TSII1	19.81	20.39
	TSII2	15.26	16.41
5	**TS1**	8.89	10.39
	TS3	9.58	11.01
6	**TS1**	4.09	5.97
	TS2	6.00	7.98
7	**TS1**	6.36	7.94
8	**TS1**	7.60	9.61
	TS2	7.74	9.85
9	**TSI1**	9.01	12.34
	TSI2	14.96	17.90
	TSI3	8.85	12.03
	TSII1[a]	-	-
	TSII2	27.33	28.94
11	**TS1**	10.17	13.11
	TS2	19.42	22.07
12	**TS1**	5.37	8.86
	TS2	1.86	5.65

[a] not found.

Table S4. Calculated Structural Parameters of Some Related Compounds (at B3LYP/aug-cc-pVTZ level)

	C-C/C=C/C≡C	C-C
ethane	1.527	
ethylene	1.325	
ethyne	1.196	
propene	1.327	1.496
propyne	1.199	1.454
allene	1.300	

Table S5. Calculated IEs for Allylphosphine **3IV, 3V** and Allylphosphine-borane **9IV, 9V** (at OVGF/aug-cc-pVTZ level)

allylphosphine (**3**)		allylphosphineborane (**9**)	
IV	**V**	**IV**	**V**
9.71	9.65	10.60	10.40
10.04	10.04	10.86	10.78
11.93	11.87	11.03	11.02
12.88	13.33	11.10	11.08
12.98	12.77	13.02	12.85
14.66	14.51	13.53	13.53
15.22	15.10	14.19	14.47
16.04	16.22	15.36	14.98
18.33	18.28	16.11	15.72
		16.35	16.72
		17.29	17.06
		19.12	18.96

Table S6. Calculated Complexation Energies of PH_3-BH_3

method	$\Delta E_{complexation}$ (kJ/mol)
B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ	73.4
MP2/aug-cc-pVTZ//MP2/aug-cc-pVTZ	84.4
CBS-QB3	74.8

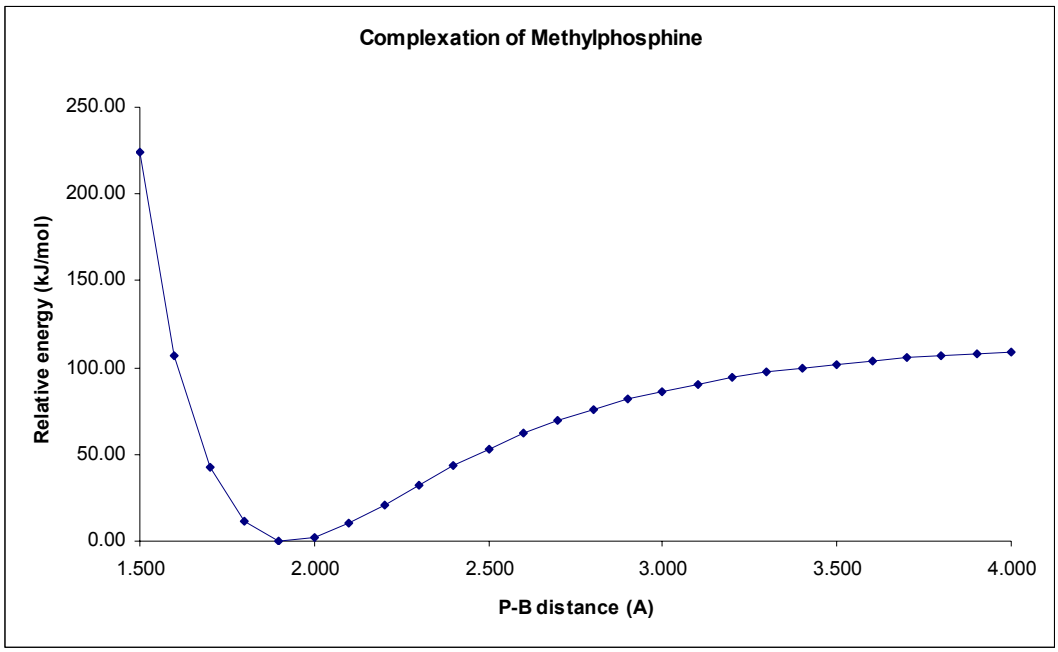


Figure S1. Energy changes in methylphosphine complexation with borane (relative energies are calculated at B3LYP/aug-cc-pVTZ level).

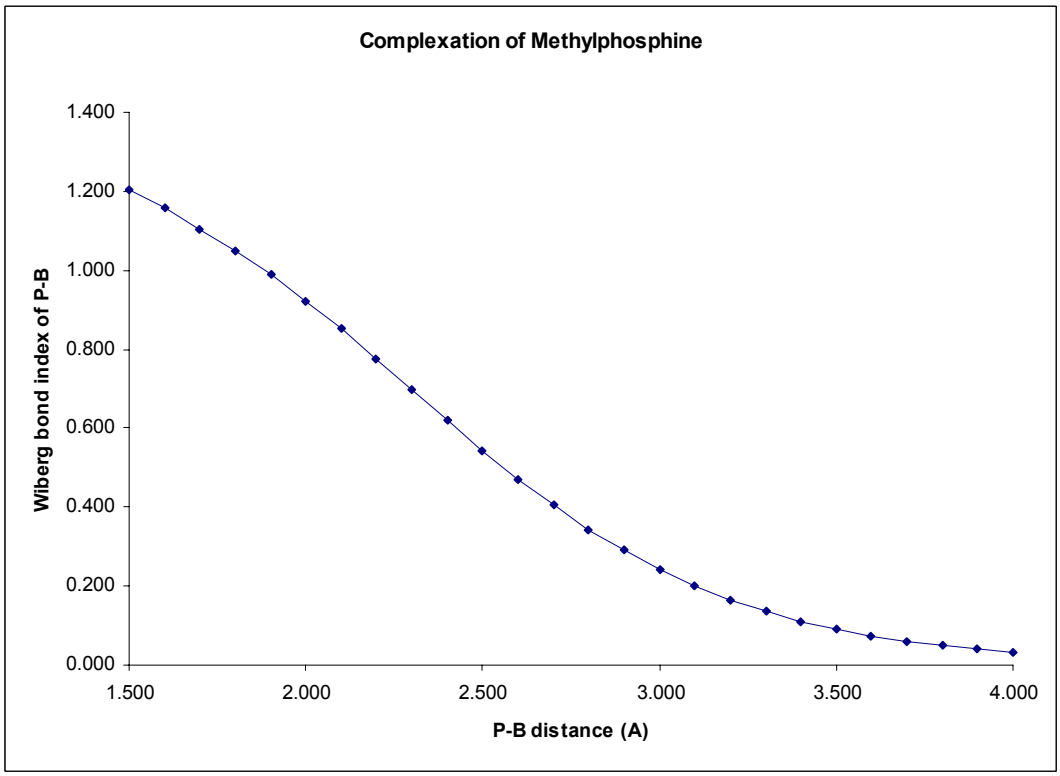


Figure S2. Wiberg index changes in methylphosphine complexation with borane (calculated at B3LYP/aug-cc-pVTZ level).

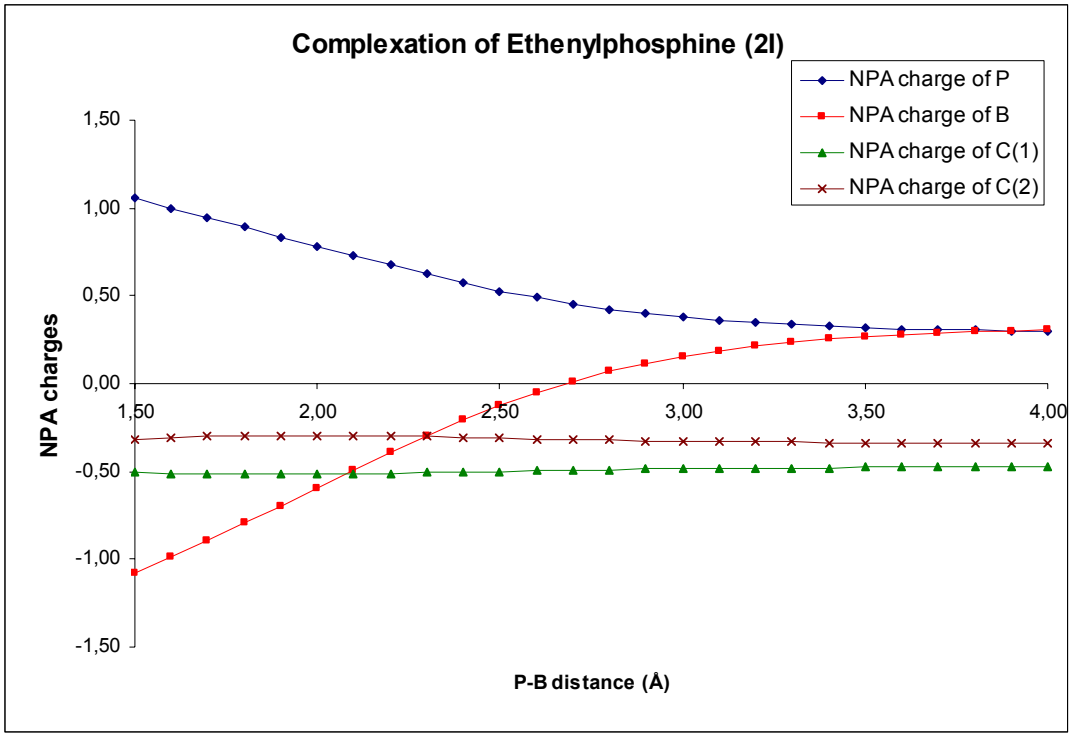


Figure S3. NPA charge changes of C, P and B atoms in methylphosphine complexation with borane (calculated at B3LYP/aug-cc-pVTZ level).

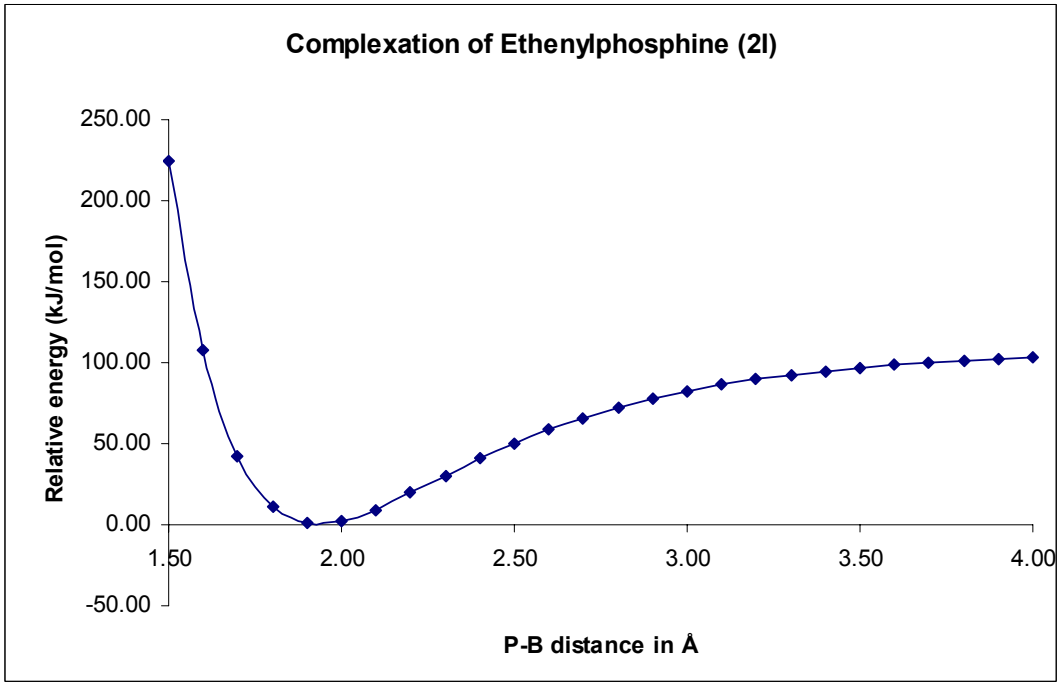


Figure S4. Energy changes in ethenylphosphine (**2l**) complexation with borane (relative energies are calculated at B3LYP/aug-cc-pVTZ level).

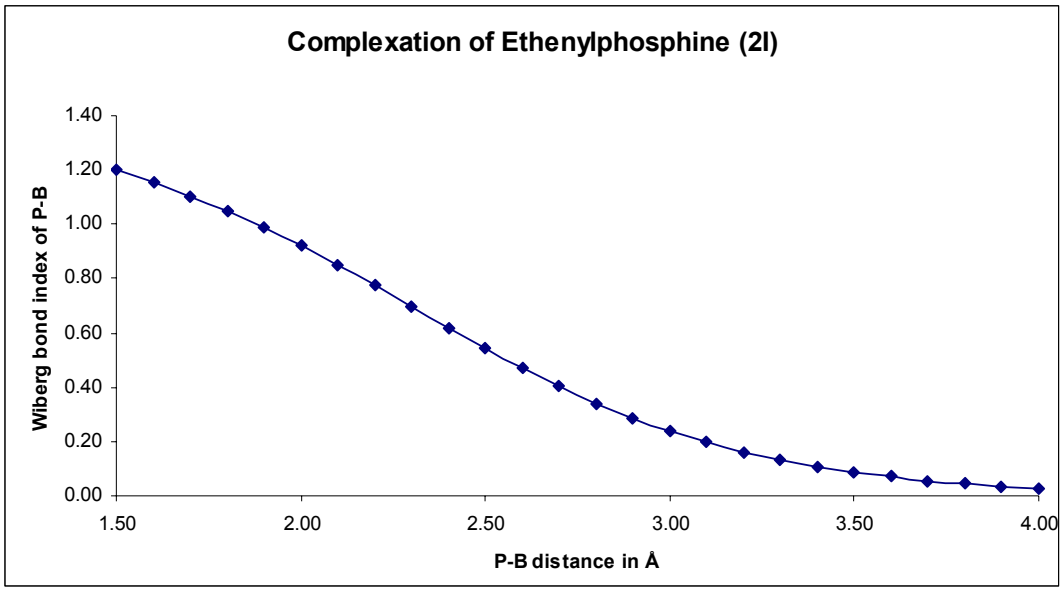


Figure S5. Wiberg index changes in ethenylphosphine (**2l**) complexation with borane (calculated at B3LYP/aug-cc-pVTZ level).

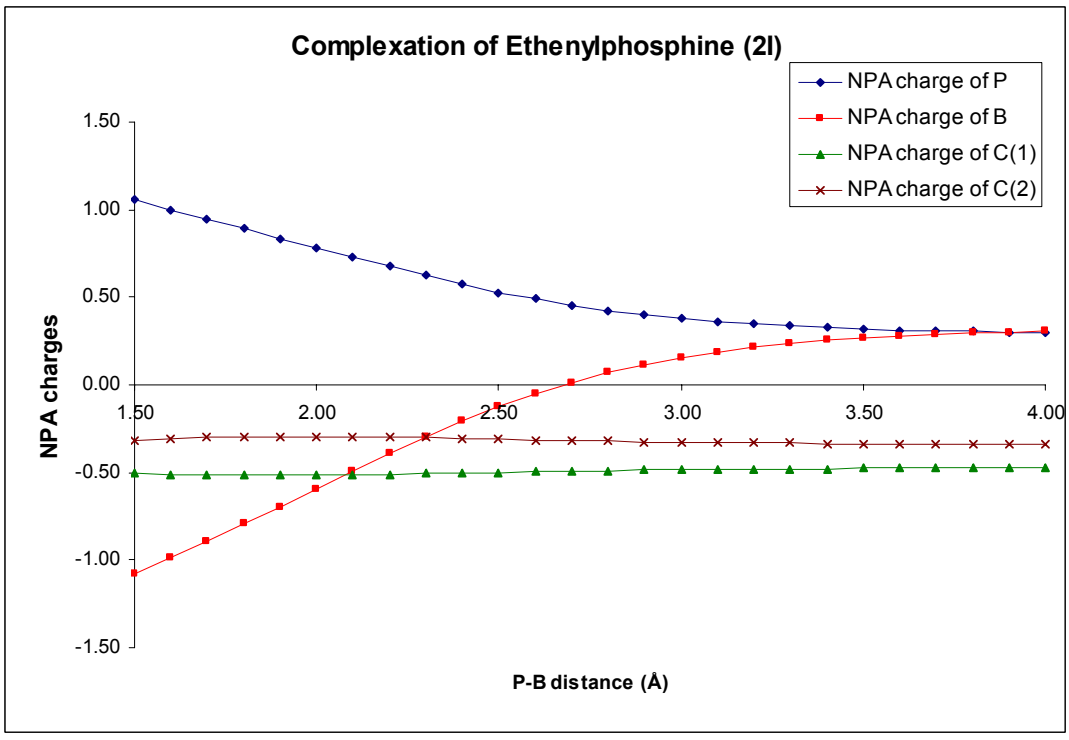


Figure S6. NPA charge changes of C, P and B atoms in ethenylphosphine (**2l**) complexation with borane (calculated at B3LYP/aug-cc-pVTZ level).

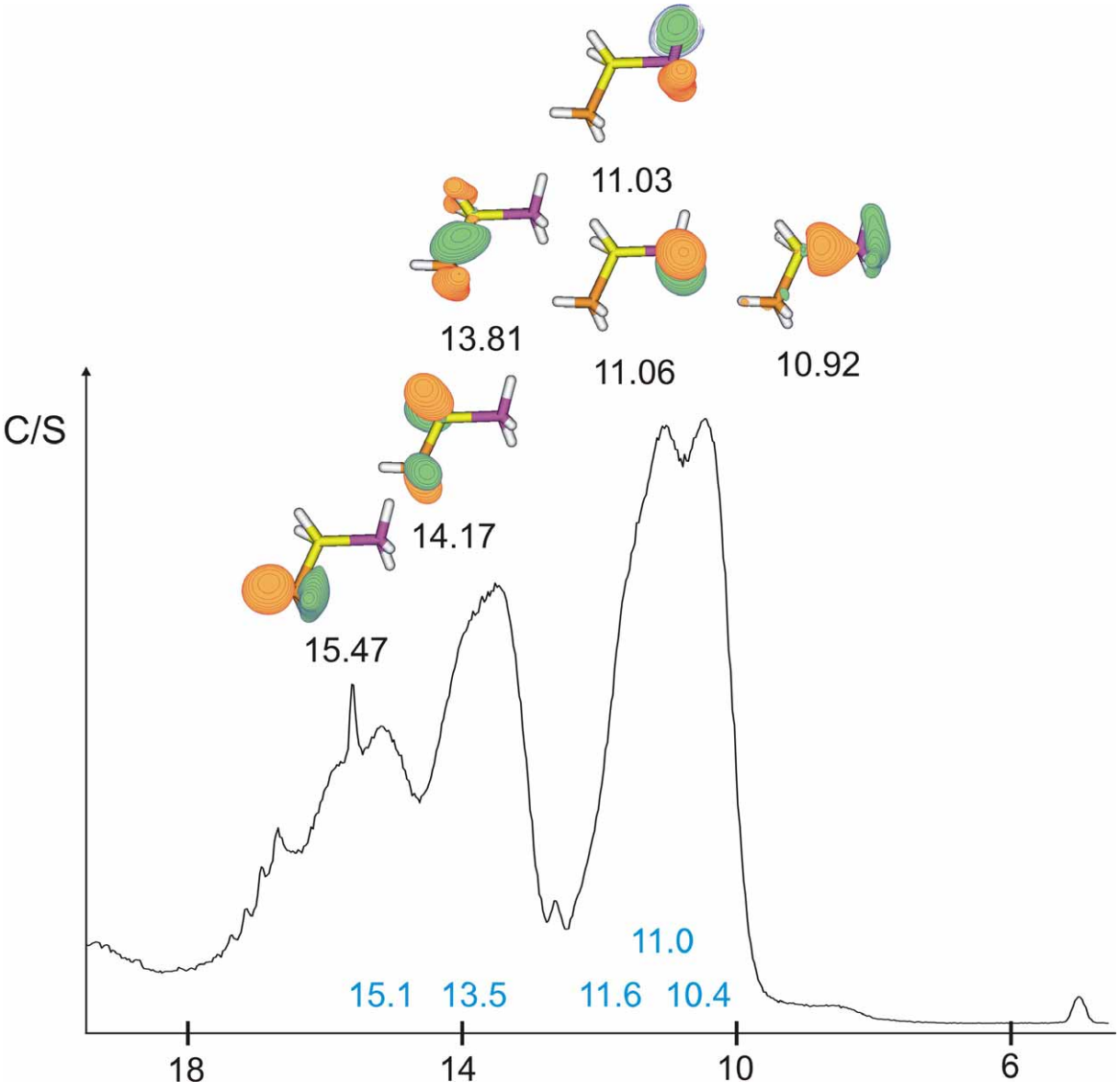


Figure S7. The observed photoelectron spectrum of methylphosphine-borane **7** and the assignment

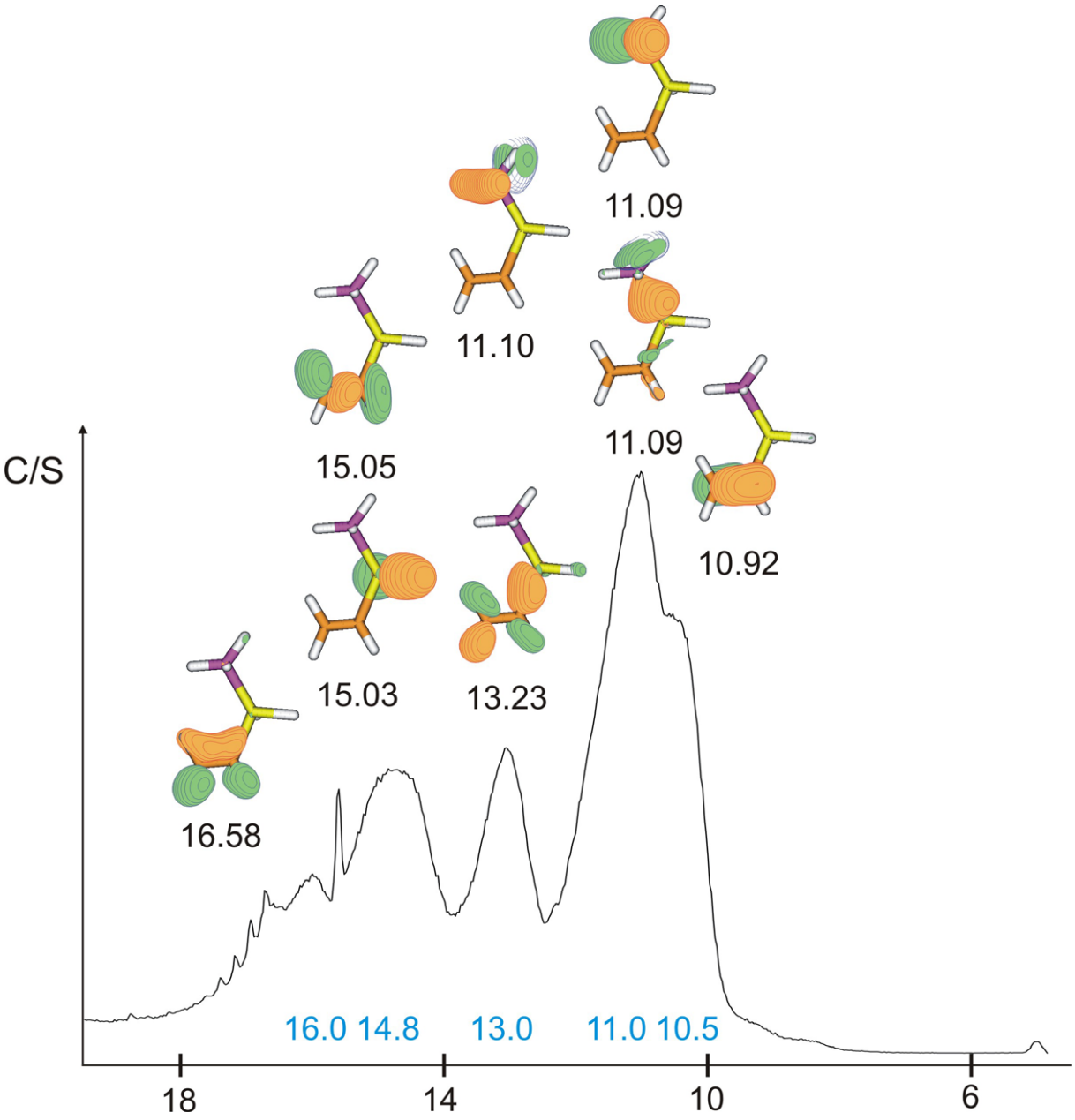


Figure S8. The observed photoelectron spectrum of ethenylphosphine-borane **8** and the assignment based on the most stable conformer

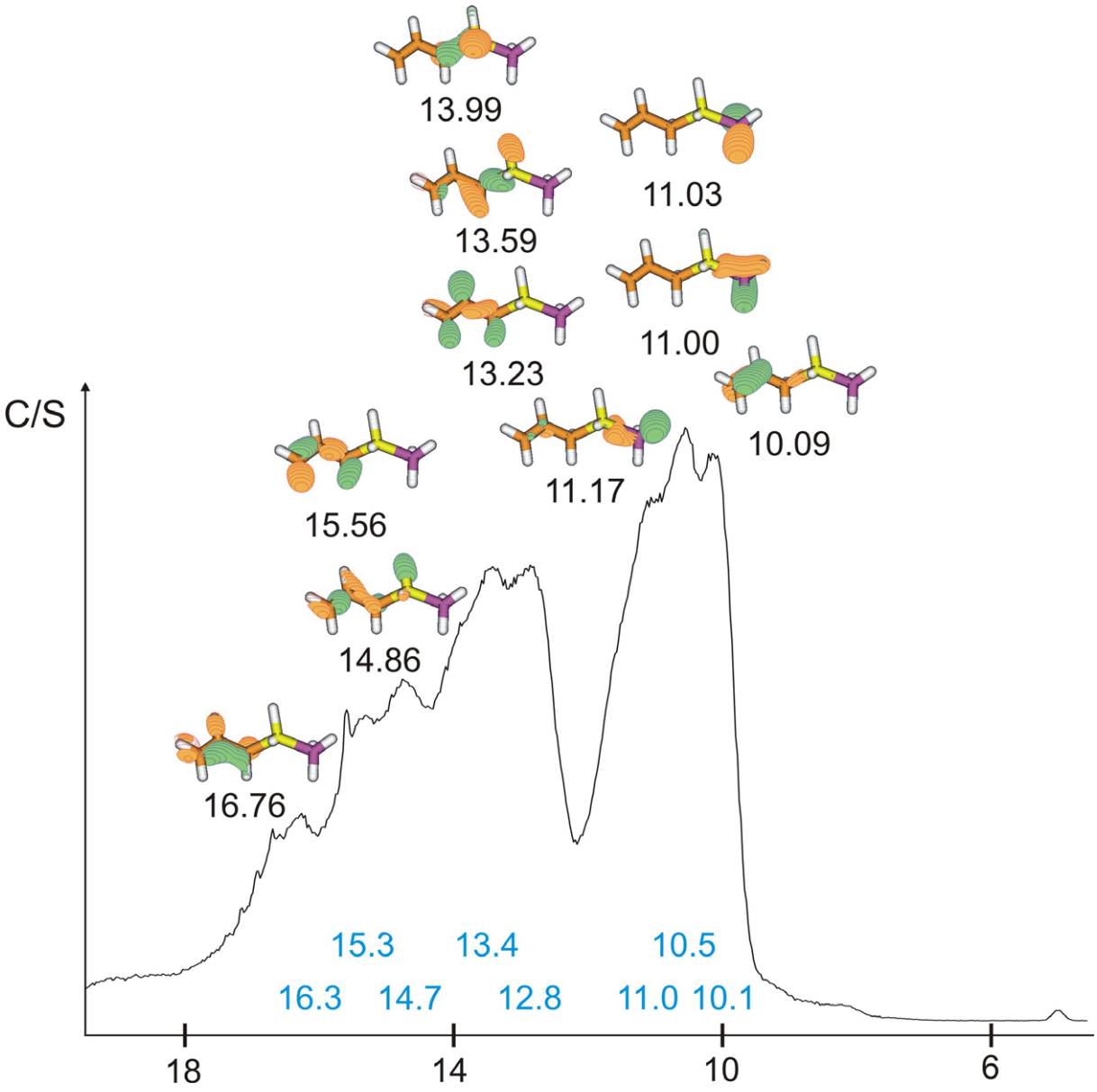


Figure S9. The observed photoelectron spectrum of allylphosphine-borane **9** and the assignment based on the most stable conformer

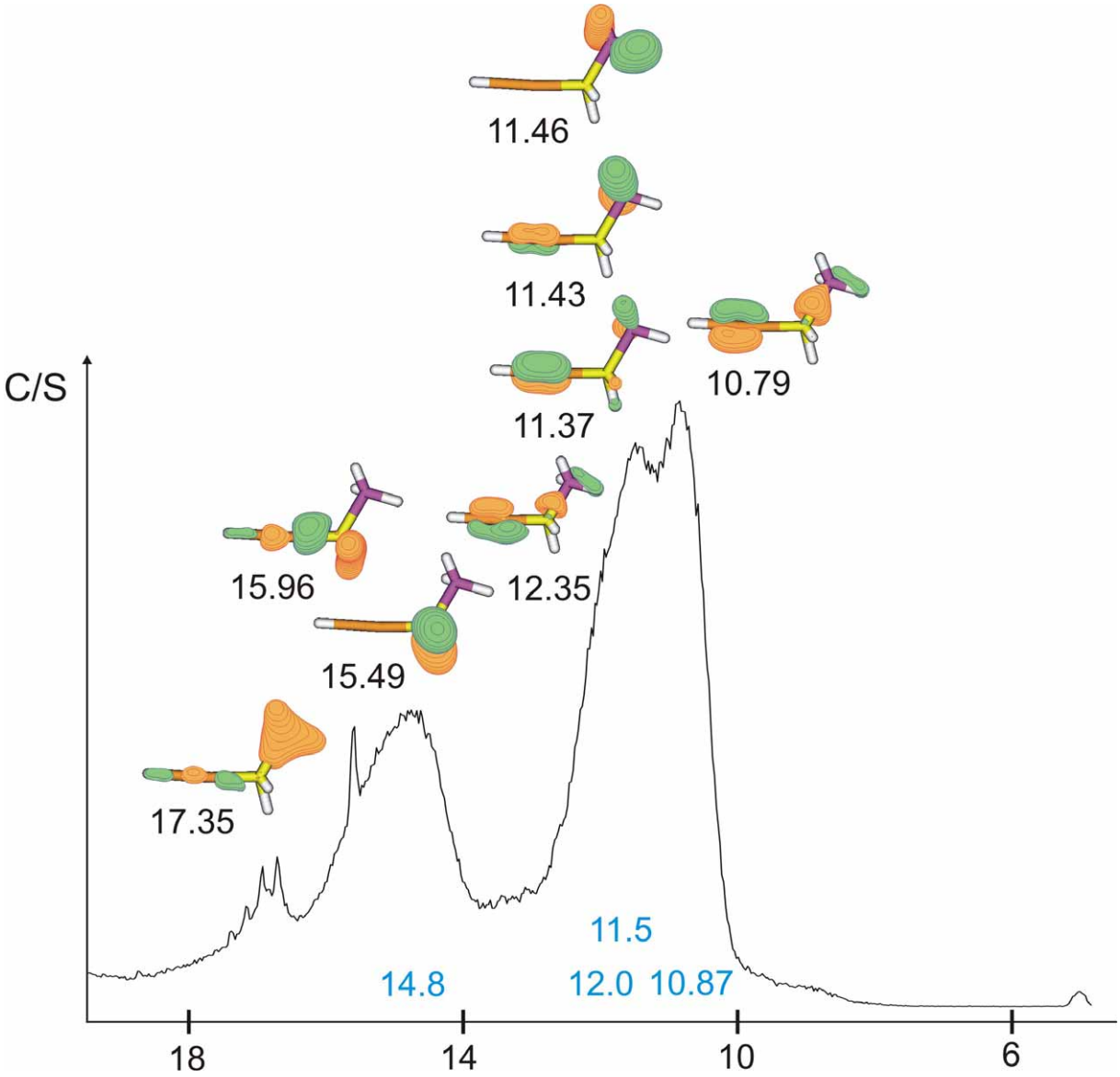


Figure S10. The observed photoelectron spectrum of ethynylphosphine-borane **10** and the assignment

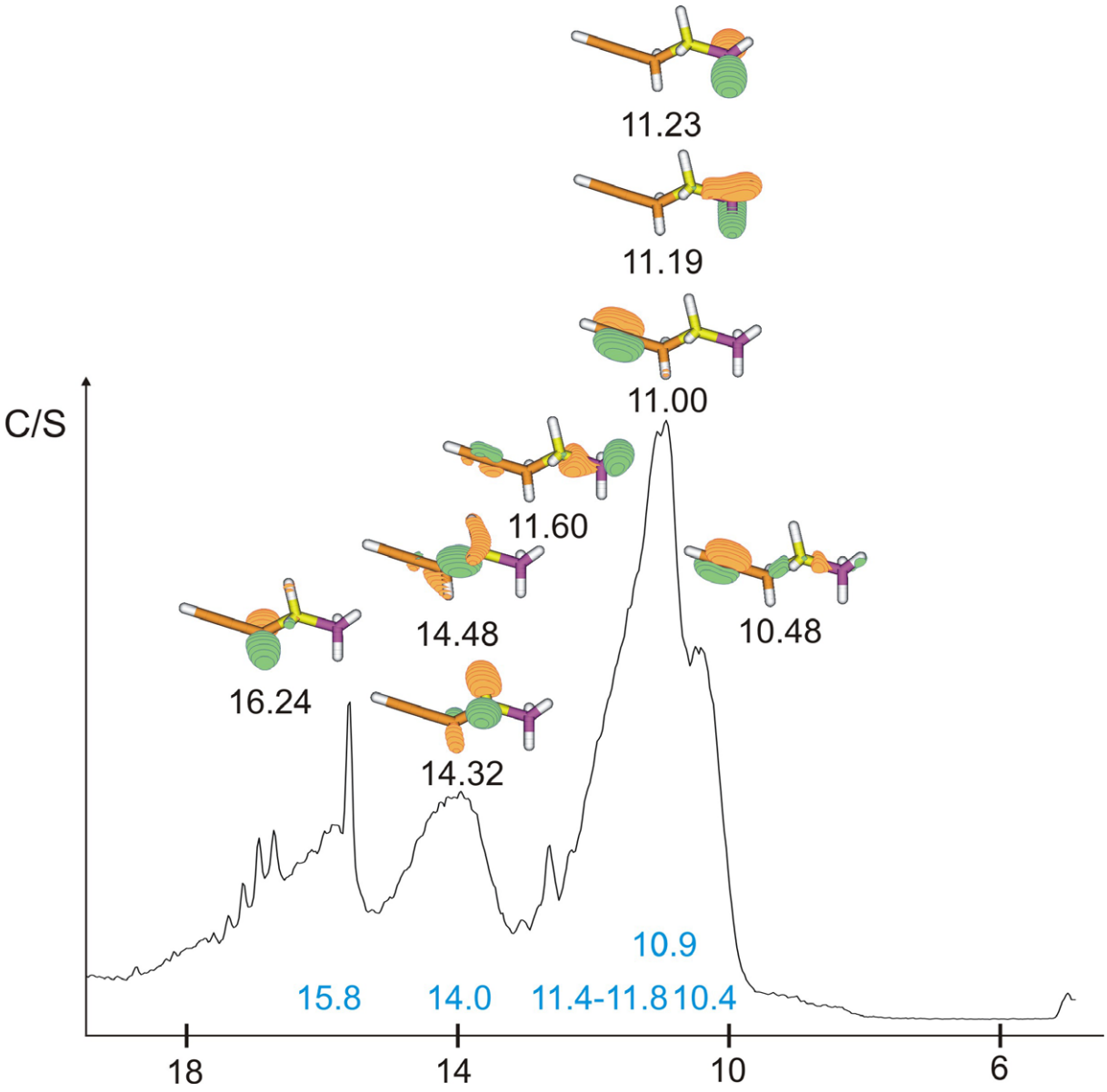


Figure S11. The observed photoelectron spectrum of propargylphosphine-borane **11** and the assignment based on the most stable conformer

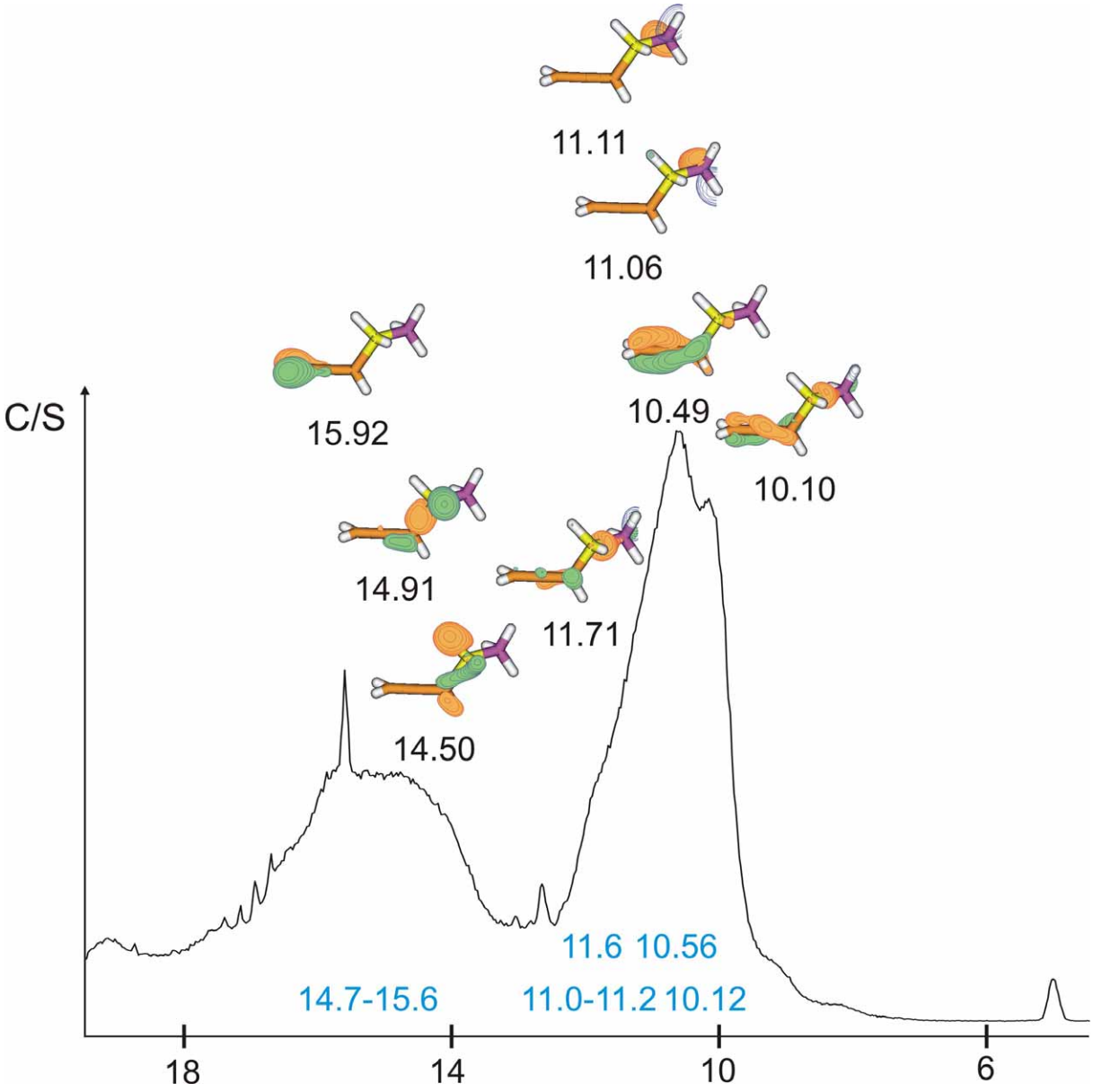


Figure S12. The observed photoelectron spectrum of allenylphosphine-borane **12** and the assignment based on the most stable conformer

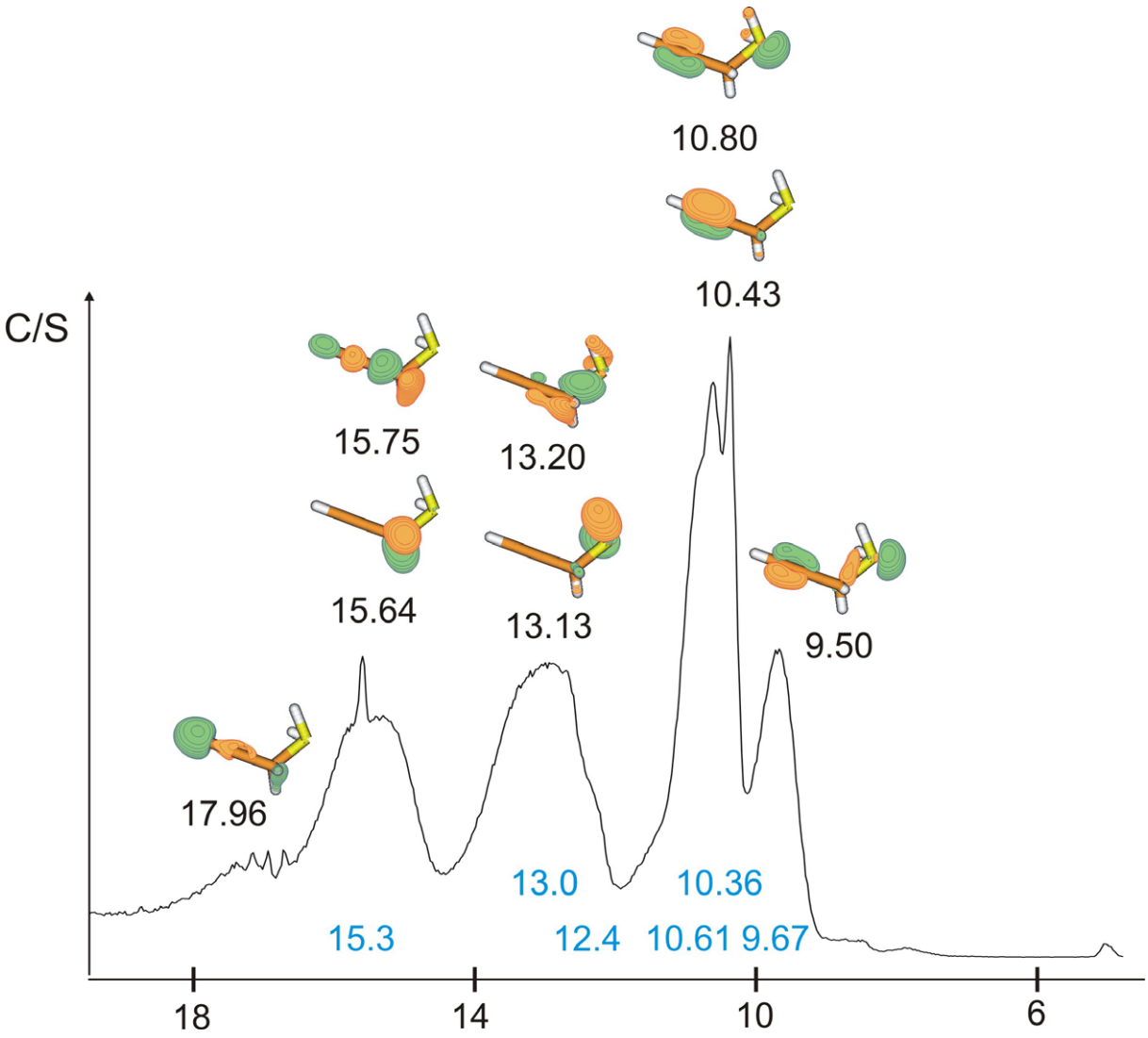


Figure S13. The observed photoelectron spectrum of propargylphosphine **5** and the assignment based on the most stable conformer