Electronic Supplementary Material (ESI) for Chemical Communications

Taming the germyliumylidene [ClGe:]$^+$ and germathionium [ClGe=S]$^+$ cations by donor-acceptor stabilization using 1,8-bis(tributylphosphazenyl)naphthalene

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Electronic Supplementary Information

A. Experimental Section

General Considerations

All experiments except the isolation of **L**·HBr (L = 1,8-bis(tri-n-butylphosphazenyl)naphthalene) were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use. The ligand 1,8-bis(tri-n-butylphosphazenyl)naphthalene (**1**) was prepared according to literature. [1] Solution state ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker spectrometers ARX200 and AV400, respectively. Elemental analyses were performed on a Flash EA 1112 CHNS Analyzer by the analytical labor, and high-resolution ESI-MS were measured on a Thermo Scientific LTQ orbitrap XL by MS-Service in the Institute of Chemistry, Technical University of Berlin, Germany.

Single-Crystal X-ray Structure Determination
Crystals were each mounted on a glass capillary in per-fluorinated oil and measured in a cold N_2 flow. The data of **2** and **3** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo-Kα-radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 [2] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. CCDC –902734, 902735 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk./data_request/cif.

Compound 2 To a solution of the ligand 1,8-bis(tri-n-butylphosphazenyl)naphthalene (**1**) (0.82 g, 1.47 mmol) in toluene (50 mL) was added $GeCl_2$·dioxane (0.34 g, 1.47 mmol) at room temperature. After the reaction mixture was stirred at that temperature for 2h, the off-white solid was filtrated and washed with toluene (10 mL). 0.62 g of **2** (0.88 mmol, 60%) was afforded. The single-crystals qualified for X-ray diffraction analysis were obtained by recrystallization of **2** in THF at -20 ºC. M.p. 158 ºC (decomp.); ^{1}H NMR (200.13 MHz, [D$_2$]dichloromethane, 25ºC): δ = 0.86 (t, ^3J (H,H) = 7 Hz, 18 H; CH_3(CH$_2$)$_3$), 1.35 – 1.62 (m, 24 H; CH$_3$(CH_2)$_2$CH$_2$), 2.51 – 2.64 (m, 12 H; CH_2(CH$_2$)$_2$CH$_3$), 6.90 (d, ^3J (H,H) = 7.5 Hz, 2 H; arom. -H), 7.37 (dd, ^3J (H,H) = 8.0 Hz, 7.5 Hz, 2 H; arom.-H), 7.58 (d. ^3J (H,H) = 8.0 Hz, 2 H; arom. -H); ^{31}P NMR (80.01 MHz, [D$_2$]dichloromethane, 25ºC): δ = 55.1 ppm; ^{13}C{^{1}H} NMR (100.61 MHz, [D$_2$]dichloromethane, 25 ºC): δ = 13.2, 23.3, 23.4, 23.7, 23.8, 24.4 (butyl), 117.7, 117.9, 124.7, 125.6, 136.5, 138.3 (arom.-C); ESI-MS: m/z (%): 559.42883 (calc. 559.43045) [M+H-GeCl$_2$]$^+$; elemental analysis calcd (%) for $C_{34}H_{60}N_2P_2GeCl_2$: C 58.2, H 8.6, N 4.0, found: C 57.94, H 8.32, N 3.90.

Conversion of [LGeCl]$^+$Cl$^-$ **2** to [LGeCl]$^+$[GeCl$_3$]$^-$ **2´**: To a solution of **2** (0.36 g, 0.51 mmol) in THF was added $GeCl_2$·dioxane (0.12 g, 0.51 mmol) at room temperature. After the reaction mixture was stirred for 2h, compound **2** converted to **2´** completely. Similarly, to a solution of **1** (0.32 g, 0.57 mmol) in THF at room temperature was added $GeCl_2$·dioxane (0.26 g, 1.15 mmol). The reaction mixture was stirred overnight and yielded pure **2´**. ^{1}H NMR (200.13 MHz, [D$_2$] dichloromethane, 25ºC): δ = 0.87 (t, ^3J (H,H) = 7 Hz, 18 H; CH_3(CH$_2$)$_3$), 1.35 – 1.60 (m, 24 H; CH$_3$(CH_2)$_2$CH$_2$), 2.36 – 2.49 (m, 12 H; CH_2(CH$_2$)$_2$CH$_3$), 6.86 (d, ^3J (H,H) = 7.5 Hz, 2 H; arom. -H), 7.39 (dd, ^3J (H,H) = 8.0 Hz, 7.5 Hz; 2 H; arom.-H), 7.61 (d. ^3J (H,H) = 8 Hz, 2 H; arom. -H); ^{31}P NMR (80.01 MHz, [D$_2$]dichloromethane, 25ºC): δ = 54.8 ppm; ^{13}C{^{1}H} NMR (100.61 MHz, [D$_2$]dichloromethane, 25 ºC): δ = 13.1, 23.2, 23.4, 23.6, 23.7, 24.4 (butyl), 117.8, 118.0, 124.9, 125.7, 136.5, 138.0 (arom.-C); negative ESI-MS: m/z (%): 178.82687 (calc. 178.82719) [GeCl$_3$]$^-$.

Compound 3 To a solution of **2** (0.72 g, 1.03 mmol) in THF (30 mL) at room temperature was added elemental sulphur (0.033 g, 1.03 mmol). The reaction mixture was stirred for 2h at this temperature. All volatiles were then removed under vacuum, and the residue was washed with toluene (20 mL), which afforded 0.30 g of **3** as yellow colored solid (0.41 mmol, 40%). The single crystals qualified for X-ray analysis were obtained by recrystallization of **3** in THF at low temperature (-20 ºC). M.p. 184 ºC (decomp.); ^{1}H NMR (200.13 MHz, [D$_8$]THF, 25ºC): δ = 0.87 (t, ^3J (H,H) = 7 Hz, 18 H; -(CH$_2$)$_3$CH_3), 1.40 – 1.70 (m, 24 H; -(CH_2)$_3$CH$_3$), 3.03 – 3.13 (m, 6 H; -(CH_2)$_3$CH$_3$), 3.36 – 3.46 (m, 6 H; (CH_2)$_3$CH$_3$), 7.52 (dd, ^3J (H,H) = 8.0 Hz, 7.5 Hz; 2 H; arom. -H), 7.61 (d, ^3J (H,H) = 8.0 Hz, 2 H; arom.-H), 7.68 (d. ^3J (H,H) = 7.5 Hz, 2 H; arom. -H); ^{31}P NMR (80.01 MHz, [D$_8$]THF, 25ºC): δ = 65.3 ppm; ^{13}C{^{1}H} NMR (100.61 MHz, [D$_8$]THF, 25 ºC): δ = 13.9, 24.3, 24.5, 24.7, 24.8, 24.9, 26.4 (butyl), 122.1, 122.2, 125.9, 127.2, 137.0, 139.3 (arom.-C); ESI-MS: m/z (%): 699.28381 (calc. 699.28473) [M-Cl]$^+$; elemental analysis calcd (%) for $C_{34}H_{60}N_2P_2GeSCl_2$: C 55.6, H 8.2, N 3.8, S 4.4, found: C 55.95, H 8.44, N 3.89, S 4.48.

Crystallographic data for 2

Empirical formula	C38 H68 Cl2 Ge N2 O P2	
Formula weight	774.37	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	p21/n	
Unit cell dimensions	a = 12.4821(7) Å	α= 90°.
	b = 19.3868(8) Å	β= 103.496(6)°.
	c = 19.0651(12) Å	γ = 90°.
Volume	4486.1(4) $Å^3$	
Z	4	
Density (calculated)	1.147 Mg/m^3	
Absorption coefficient	0.901 mm^{-1}	
F(000)	1656	
Crystal size	0.37 x 0.21 x 0.09 mm^3	
Theta range for data collection	3.49 to 25.00°.	
Index ranges	-14<=h<=12, -23<=k<=22, -17<=l<=22	
Reflections collected	18231	
Independent reflections	7853 [R(int) = 0.0518]	
Completeness to theta = 25.00°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.82277	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7853 / 38 / 441	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0606, wR2 = 0.1229	
R indices (all data)	R1 = 0.0853, wR2 = 0.1325	
Largest diff. peak and hole	0.549 and -0.524 $e.Å^{-3}$	

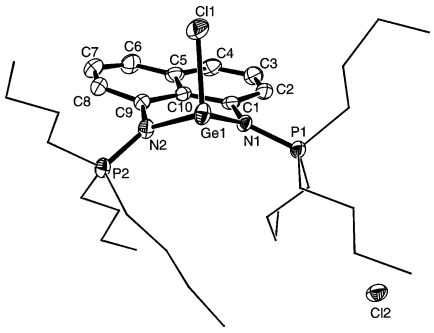


Figure S1. Molecular structure of compound **2**. Thermal ellipsoids are drawn at 50% probability level. H atoms and one THF molecule are omitted for clarity.

Table S1. Selected interatomic distances and angles of compound **2**

Interatomic distances (Å)		Angles (º)	
Ge(1)-N(2)	1.960(3)	N(1)-Ge(1)-N(2)	88.3(1)
Ge(1)-N(1)	1.981(3)	Cl(1)-Ge(1)-N(2)	96.2(1)
Ge(1)-Cl(1)	2.278(1)	Cl(1)-Ge(1)-N(1)	95.4(1)
P(1)-N(1)	1.653(3)	C(1)-N(1)-P(1)	120.0(2)
P(2)-N(2)	1.640(3)	C(1)-N(1)-Ge(1)	120.4(2)
N(1)-C(1)	1.426(5)	P(1)-N(1)-Ge(1)	119.1(2)
N(2)-C(8)	1.436(5)	N(1)-C(1)-C(9)	121.7(3)
C(1)-C(9)	1.440(5)	C(8)-N(2)-P(2)	119.1(3)
C(8)-C(9)	1.435(5)	C(8)-N(2)-Ge(1)	118.6(2)
		P(2)-N(2)-Ge(1)	122.2(2)
		N(2)-C(8)-C(9)	119.4(3)
		C(1)-C(9)-C(8)	125.8(3)

Crystallographic data for **3**

Empirical formula	C38 H68 Cl2 Ge N2 O P2 S	
Formula weight	806.43	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.5878(7) Å	α= 90°.
	b = 17.8076(10) Å	β= 105.550(4)°.
	c = 21.8753(14) Å	γ = 90°.
Volume	4348.8(5) $Å^3$	
Z	4	

Density (calculated)	1.232 Mg/m^3
Absorption coefficient	0.979 mm^{-1}
F(000)	1720
Crystal size	0.31 x 0.13 x 0.11 mm^3
Theta range for data collection	3.57 to 25.00°.
Index ranges	-13<=h<=13, -20<=k<=21, -26<=l<=26
Reflections collected	30133
Independent reflections	7643 [R(int) = 0.0655]
Completeness to theta = 25.00°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.28311
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7643 / 0 / 430
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1313
R indices (all data)	R1 = 0.0830, wR2 = 0.1475
Largest diff. peak and hole	1.520 and -1.240 $e.Å^{-3}$

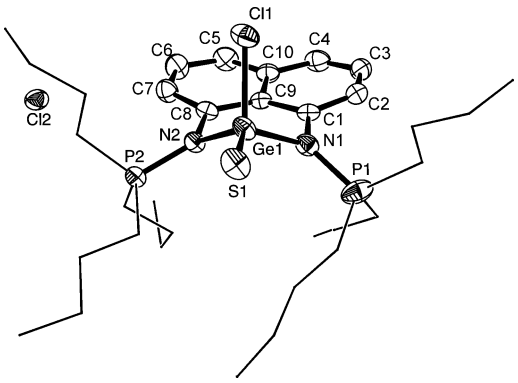


Figure S2. Molecular structure of compound **3**. Thermal ellipsoids are drawn at 50% probability level. H atoms and one THF molecule are omitted for clarity.

Table S2. Selected interatomic distances and angles of compound **3**

Interatomic distances (Å)		Angles (º)	
Ge(1)-N(1)	1.897(4)	N(1)-Ge(1)-N(2)	93.0(2)
Si(1)-N(2)	1.900(3)	N(1)-Ge(1)-S(1)	120.9(1)
Si(1)-Cl(1)	2.181(1)	N(2)-Ge(1)-S(1)	123.6(1)
Si(1)-S(1)	2.066(1)	Cl(1)-Ge(1)-N(1)	101.6(1)
P(1)-N(1)	1.666(4)	Cl(1)-Ge(1)-N(2)	99.9(1)
P(2)-N(2)	1.669(3)	S(1)-Ge(1)-Cl(1)	113.5(1)

C(1)-N(1)	1.444(5)	C(1)-N(1)-P(1)	118.2(3)
N(2)-C(8)	1.455(5)	C(1)-N(1)-Ge(1)	113.4(3)
C(8)-N(2)	1.455(5)	C(8)-N(2)-P(2)	118.8(3)
C(1)-C(9)	1.427(6)	P(1)-N(1)-Ge(1)	128.4(2)
C(8)-C(9)	1.439(6)	C(8)-N(2)-Ge(1)	113.4(2)
		P(2)-N(2)-Ge(1)	126.8(2)
		N(1)-C(1)-C(9)	120.9(4)
		C(9)-C(1)-N(1)	120.9(4)
		C(9)-C(8)-N(2)	120.7(4)
		C(1)-C(9)-C(8)	126.0(4)

B. Theoretical Calculations

DFT calculations of the model compound **2**$^{+}$ were performed at the B3LYP level using the 6-31G(d) basis set with the GAUSSIAN-03 program package.[3] The structure obtained by X-ray analysis was used as the input for the calculations. Optimized structures and molecular orbitals of **2**$^{+}$ are shown in Figure S3 and S4, respectively. The Cartesian coordinates of the optimized structure are shown in Table 3. Optimized structure of model compound was obtained without symmetry constraints. The NBO approach was used to calculate the orbital populations, Wiberg Bond Indices (WBI), and Natural Population Analysis (NPA).

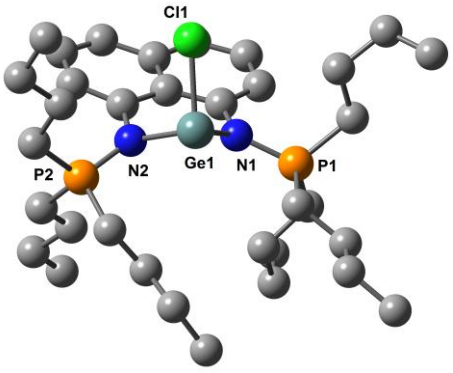
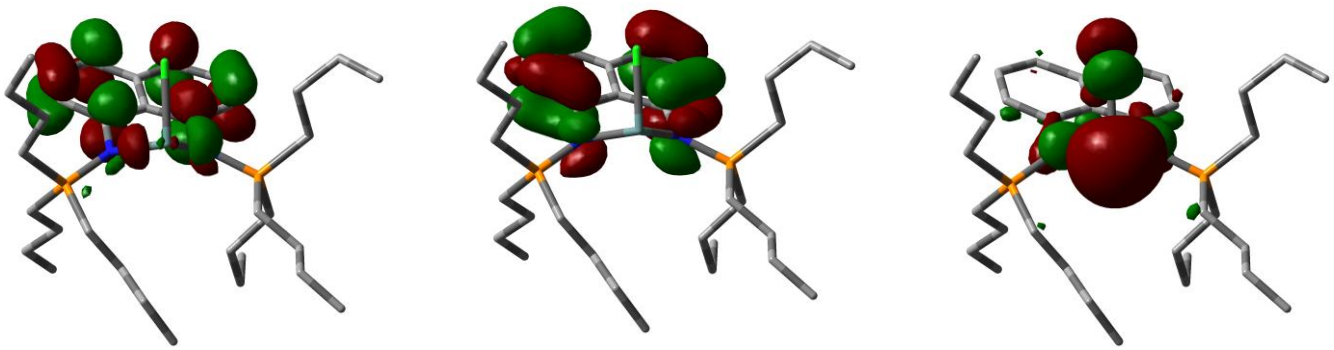


Figure S3. Optimized structure of compound **2**$^{+}$.



LUMO (-0.1288 eV) HOMO (-0.2839 eV) HOMO-1 (-0.3145 eV)

Figure S4. Molecular orbitals of compound **2**$^{+}$.

Table S3. Cartesian coordinates (x, y, z) for the optimized structure of **2**$^{+}$.

Ge	-0.06980666	-1.39603913	-0.55040319
Cl	-0.56783721	-3.11887343	0.87462762
P	2.50867181	0.07151237	0.46797254
N	0.90864773	-0.25165285	0.78601900
C	0.35160609	-0.02759630	2.08728724
P	-2.71540143	0.14920809	-1.32749766
N	-1.67511289	-0.26864599	-0.10868177
C	1.17971573	0.14127691	3.18968653
H	2.25189347	0.04868617	3.08104151
C	0.69119575	0.38600707	4.48634160
H	1.39381958	0.51842588	5.30363998
C	-0.65947581	0.41905181	4.70576563
H	-1.06175178	0.58032112	5.70133753
C	-1.56192636	0.20759585	3.63254836
C	-2.95243757	0.18243118	3.91835352
H	-3.27324873	0.34089609	4.94358534
C	-3.86236665	-0.07420856	2.92769575
H	-4.92406837	-0.13775721	3.14641592
C	-3.41103390	-0.26991409	1.60915911
H	-4.14578340	-0.51788368	0.85254584
C	-2.07163447	-0.18565840	1.26011459
C	-1.07935412	0.01083227	2.28705622
C	3.72293878	-1.04986649	1.29558264
H	4.63495275	-1.01894914	0.68782258
H	3.99316480	-0.63832712	2.27447337
C	3.19660970	-2.49213925	1.44181293
H	2.91647940	-2.89215857	0.45760031
H	2.27573549	-2.47972024	2.03350350
C	2.80042836	-0.18441828	-1.32927980
H	2.73964683	-1.26291248	-1.51323542
H	1.96949240	0.26067441	-1.88280508
C	4.14540650	0.36498147	-1.84571081
H	4.15804943	1.45952180	-1.76871741
H	4.97671368	-0.00030003	-1.22875847
C	4.40114206	-0.04130135	-3.30607845
H	3.56922122	0.31198035	-3.93052128
H	4.39891214	-1.13701281	-3.38031162
C	5.72300004	0.51145728	-3.84702306
H	5.73979490	1.60730916	-3.81655711
H	5.87841109	0.20508214	-4.88631851
H	6.57611033	0.14728606	-3.26262768
C	2.93000094	1.81133751	0.88050211
H	2.88337389	1.91287181	1.96754334
H	3.97785735	1.96521423	0.59230638
C	2.01095579	2.84461985	0.20348576

H	2.07002366	2.72709362	-0.88658887
H	0.97129852	2.63633487	0.48560984
C	2.36841584	4.29822113	0.56499428
H	1.74390794	4.95812740	-0.05038917
H	3.40672880	4.50127528	0.26871415
C	2.17003054	4.65513772	2.04211183
H	1.14308423	4.44737709	2.36605017
H	2.36356246	5.71944523	2.20995601
H	2.84696364	4.09801811	2.69983992
C	-1.74355781	0.34790166	-2.87109845
H	-1.26295106	-0.61570882	-3.07713649
H	-2.48518783	0.50276654	-3.66551754
C	-0.69879829	1.47400721	-2.88825624
H	-1.20173478	2.44792194	-2.85185357
H	-0.07922874	1.41547123	-1.98428311
C	0.18001236	1.40747915	-4.14611768
H	0.72730793	0.45422219	-4.14865310
H	-0.46432534	1.38925135	-5.03530815
C	1.16067763	2.57863507	-4.25607473
H	0.63142283	3.53743709	-4.30157559
H	1.77393741	2.49577813	-5.15921404
H	1.83988626	2.61700975	-3.39492790
C	-3.99061676	-1.11642526	-1.76032767
H	-4.83765700	-1.00680449	-1.07331804
H	-4.36795026	-0.85637259	-2.75881463
C	-3.46724644	-2.56455120	-1.72774885
H	-2.61051961	-2.67457152	-2.40742256
H	-3.09100358	-2.79450526	-0.72411807
C	-4.55552181	-3.57538483	-2.11950271
H	-5.40910141	-3.46586945	-1.43631892
H	-4.93260073	-3.33589661	-3.12351069
C	-4.05295123	-5.02182107	-2.08673316
H	-3.22491120	-5.17102549	-2.78968256
H	-4.85162695	-5.71901771	-2.35997332
H	-3.69512250	-5.29480806	-1.08766831
C	-3.62397913	1.71906601	-0.99857219
H	-3.97951290	2.05752482	-1.98201230
H	-4.51863181	1.46407337	-0.42105271
C	-2.84684083	2.83979873	-0.28455730
H	-2.48996983	2.47222035	0.68343361
H	-1.95761453	3.11590591	-0.86326485
C	-3.72130018	4.08507780	-0.07197531
H	-4.60642929	3.80797888	0.51654858
H	-4.09560074	4.44028851	-1.04212192
C	-2.96998824	5.21744380	0.63483537
H	-2.60862121	4.89988452	1.62005881
H	-3.61914954	6.08637478	0.78262579
H	-2.10302451	5.54670363	0.04916869

C	4.21780670	-3.43832108	2.09654461
H	4.49551554	-3.04374903	3.08385723
H	3.71035417	-4.39231558	2.28324356
C	5.47962581	-3.69527454	1.26566199
H	5.22687943	-4.09417533	0.27545832
H	6.12569260	-4.42740025	1.76066801
H	6.07714545	-2.78699930	1.12037742

C. References

1. Y. Xiong, S. Yao, S. Inoue, E. Irran, M. Driess. *Angew. Chem. Int. Ed*. 2012, in press.
2. G. M. Sheldrick, *SHELX-97 Program for Crystal Structure Determination*, Universität Göttingen (Germany) **1997**.
3. a) Gaussian 03, Revision E.01, 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; b) A. D. Becke, *J. Chem. Phys*. **1993**, *98*, 5648; c) C. Lee, W. Yang, R. G. Parr*, Phys. Rev*. B **1988**, *37*, 785 ; d)B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett*. **1989**, *157*, 200.