Reactions of a Quintuply Bonded Chromium Dimer with Alkynes

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Supporting information

Contents:

General. All manipulations of compounds were carried out using standard Schlenk, high vacuum line, and glovebox techniques under an atmosphere of N_2. Solvents were purchased from Fisher Scientific, degassed, and dried by passing through activated alumina. THF-d_8 and C_6D_6 was purchased from Cambridge Isotopes Laboratory and stored under vacuum over Na/K alloy. All other reagents were purchased from Aldrich or Acros and dried using standard procedures, when necessary.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer and were referenced to the residual protons (or ^{13}C nuclei) of the solvents. FTIR spectra were recorded on a Magna-IR E. S. P. 560 spectrometer. UV/vis spectra were obtained using a Thermo UV-1 spectrophotometer. Elemental analyses were performed by Robertson Microlit Laboratories.

Synthesis and characterization of Cr Complexes

Preparation of [^{H}L^{iPr}Cr]$_2$(μ-η^1:η^1-MeCCMe) (2a): [^{H}L^{iPr}Cr]$_2$ (**1**) (0.200g, 0.234mmol) was dissolved in 50ml diethyl ether or toluene in an ampoule with a stir bar. The ampoule was attached to a vacuum manifold. Approximately 0.1ml of 2-butyne (0.069g, 1.280mmol) was vacuum transferred over. The color of the solution changed from green to deep-purple immediately. The mixture was stirred one hour at room temperature. The solvent was removed and the ampoule was brought back in the dry box, where the residue was extracted with diethyl ether. Concentration of the filtrate and cooling to -30°C yielded dark purple crystals of **2a** (0.164g, 77% yield). ^{1}H NMR (toluene-d_8, 233K): 6.76 (2H, d, aryl, *J*HH = 7 Hz), 6.17 (2H, d, aryl, *J*HH = 7 Hz),

6.64 (2H, d, aryl, *J*HH = 7 Hz), 6.49 (2H, d, aryl, *J*HH = 7 Hz), 3.78 (2H, m, iPr, *J*HH = 6 Hz), 3.53 (2H, m, iPr, *J*HH = 6 Hz), 3.24 (2H, m, iPr, *J*HH = 6 Hz), 2.74 (6H, s, 2-butyne), 2.44 (2H, m, iPr, *J*HH = 6 Hz), 1.43 (12H, d, iPr, *J*HH = 6 Hz), 1.31 (12H, d, iPr, *J*HH = 6 Hz), 1.18 (6H, d, iPr, *J*HH = 6 Hz), 1.03 (6H, d, iPr, *J*HH = 6 Hz), 0.34 (6H, d, iPr, *J*HH = 6 Hz), 0.07 (6H, d, iPr, *J*HH = 6 Hz) ppm. ^{1}H NMR (toluene-d_8, 303K): 6.62 (br), 3.79 (br), 3.56 (br), 2.74 (s, 2-butyne), 1.22 (br), 0.27 (br), 0.04 (br) ppm. IR (KBr): 3058 (w), 2960 (s), 2925 (s), 2865 (m), 1531 (s), 1462 (s), 1432 (s), 1382 (w), 1360 (w), 1319 (m), 1268 (m), 1254 (m), 1241 (s), 1218 (m), 1205 (m), 1181 (s), 1109 (m), 1056 (w), 1042 (w), 928 (w), 798 (m), 754 (s). Anal. Calcd. for $C_{56}H_{78}N_4Cr_2$: C, 73.81; H, 8.63; N, 6.15. Found: C, 73.37; H, 8.48; N, 6.00.[a] UV/Vis (toluene): λ_{max} (ε) = 498 (5723 M^{-1} cm^{-1}), 707 (5638 M^{-1} cm^{-1}). M. p.: 196°C (dec).

Preparation of [^{H}L^{iPr}Cr]$_2$(μ-η^1:η^1-EtCCEt)·Et$_2$O (2b): [^{H}L^{iPr}Cr]$_2$ (**1**) (0.200g, 0.234mmol) was dissolved in 50ml diethyl ether or toluene in an ampoule with a stir bar. The ampoule was attached to a vacuum manifold. Approximately 0.1ml of 3-hexyne (0.072g, 0.877mmol) was vacuum transferred over. The color of the solution changed from green to deep-purple immediately. The mixture was stirred one hour at room temperature. The solvent was removed and the ampoule was brought back in the dry box, the residue was extracted with diethyl ether. Concentration of the filtrate and cooling to -30°C yielded dark purple crystals of **2b** (0.153g, 70% yield). ^{1}H NMR (C_6D_6): 8.34 (1H, d, aryl, , *J*HH = 6 Hz), 7.26 (1H, d, aryl, *J*HH = 6 Hz), 7.00 (4H, t, aryl, *J*HH = 7 Hz), 6.92 (1H, d, aryl, *J*HH = 7 Hz), 6.73 (2H, d, aryl, *J*HH = 7 Hz), 6.36 (2H, d, aryl, *J*HH = 7 Hz), 5.74 (1H, s, backbone), 4.37 (1H, m, iPr), 4.27 (1H, m, iPr), 3.80 (1H, m, iPr), 3.57 (1H, m, iPr), 3.37 (1H, m, iPr), 3.17 (1H, m, iPr), 3.05 (1H, m, iPr), 2.82 (1H, m, iPr), 2.59 (2H, m, EtCCEt), 2.34 (2H, m, EtCCEt), 1.64 (3H, d, *J*HH = 6 Hz, CH_3), 1.57 (3H, d, *J*HH = 6 Hz, CH_3), 1.44 (3H, d, *J*HH = 6 Hz, CH_3), 1.39 (3H, d, *J*HH = 6 Hz, CH_3), 1.36 (3H, d, *J*HH = 6 Hz, CH_3), 1.30 (3H, d, *J*HH = 6 Hz, CH_3), 1.25 (3H, d, *J*HH = 6 Hz, CH_3), 1.21 (3H, d, *J*HH = 6 Hz, CH_3), 1.18 (3H, d, *J*HH = 6 Hz, CH_3), 1.15 (3H, d, *J*HH = 6 Hz, CH_3), 1.09 (3H, d, *J*HH = 6 Hz, CH_3), 0.97 (3H, t, *J*HH = 6 Hz, CH_3), 0.77 (3H, d, *J*HH = 6 Hz, CH_3), 0.74 (3H, d, *J*HH = 6 Hz, CH_3), 0.68 (3H, d, *J*HH = 6 Hz, CH_3), 0.25 (3H, d, *J*HH = 6 Hz, CH_3), 0.03 (3H, d, *J*HH = 6 Hz, CH_3), -0.11 (3H, t, *J*HH = 6 Hz, CH_3) ppm. IR (KBr): 3058 (w), 2960 (s), 2925 (s), 2864 (m), 1580 (w), 1539 (w), 1463 (m), 1383 (w), 1370 (w), 1318 (w), 1255 (w), 1240 (w), 1179 (w), 1108 (w), 1019 (w), 798 (m), 754 (s), 698 (m). Anal. Calcd. for $C_{62}H_{92}N_4OCr_2$: C, 73.48; H, 9.15; N, 5.53. Found: C, 72.58; H, 8.68; N, 5.98.[a] UV/Vis (toluene): λ_{max} (ε) = 457 (3353 M^{-1} cm^{-1}), 501 (3200 M^{-1} cm^{-1}), 709 (6393 M^{-1} cm^{-1}). M. p.: 190°C (dec).

Preparation of [^{H}L^{iPr}Cr]$_2$(μ-η^1:η^1-PhCCPh) (2c): Diphenylacetylene (0.042g, 0.234mmol) was added in 50ml of diethyl ether or toluene solution of [^{H}L^{iPr}Cr]$_2$ (**1**) (0.200g, 0.234mmol). The color of the solution changed from green to deep-purple. The mixture was stirred three hours at room temperature. The solvent was removed and the residue was extracted with toluene. Concentration of the filtrate and cooling to -30°C yielded dark purple crystals of **2c** (0.174g, 82% yield). ^{1}H NMR (toluene-d_8): 7.73 (1H, d, aryl, *J*HH = 7 Hz), 7.25 (2H, t, aryl, *J*HH = 7 Hz), 7.19 (1H, d, aryl, *J*HH = 7 Hz), 6.94 (4H, t, aryl, *J*HH = 7 Hz), 6.87 (1H, d, aryl, *J*HH = 7 Hz), 6.79 (1H, d, aryl, *J*HH = 7 Hz), 6.60 (1H, d, aryl, *J*HH = 7 Hz), 6.44 (1H, d, aryl, *J*HH = 7 Hz), 4.06 (1H, m, iPr), 3.96(1H, m, iPr), 2.68 (1H, m, iPr), 2.54 (1H, m, iPr), 1.67(1H, m, iPr), 1.52 (3H, d, iPr, *J*HH = 6 Hz), 1.48 (3H,

d, iPr, *J*HH = 6 Hz), 1.43 (br), 1.35 (3H, d, iPr, *J*HH = 6 Hz), 1.23 (6H, t, iPr, *J*HH = 6 Hz), 1.16 (6H, t, iPr, *J*HH = 6 Hz), 1.09 (3H, d, iPr, *J*HH = 6 Hz), 0.93 (6H, t, iPr, *J*HH = 6 Hz), 0.73 (br), 0.43 (3H, d, iPr, *J*HH = 6 Hz), 0.33 (3H, d, iPr, *J*HH = 6 Hz), 0.13 (br), -0.13 (3H, d, iPr, *J*HH = 6 Hz) ppm. IR (KBr): 3060 (w), 2960 (s), 2923 (s), 2866 (m), 1653 (w), 1689 (w), 1461 (s), 1460 (m), 1383 (w), 1362 (w), 1320 (w), 1258 (w), 1178 (w), 1105 (w), 1057 (w), 798 (m), 754 (m), 699 (m). Anal. Calcd. for $C_{66}H_{82}N_4Cr_2$: C, 76.56; H, 7.98; N, 5.41. Found: C, 74.86; H, 8.04; N, 5.11.[a] UV/Vis (toluene): λ_{max} (ε) = 516 (5000 M^{-1} cm^{-1}), 677 (2806 M^{-1} cm^{-1}). M. p.: 183˚C (dec).

Preparation of $[^{H}L^{iPr}Cr]_2(CF_3CCCF_3)$ (3): $[^{H}L^{iPr}Cr]_2$ (**1**) (0.200g, 0.234mmol) was placed in an ampoule with a stir bar and 50mL diethyl ether and attached to a vacuum manifold. Three freeze-pump-thaw cycles were performed followed by condensation of excess hexafluoro-2-butyne (approximate 1mmol). The solution was warmed up to room temperature and stirred for 15 mins during which time the colored changed from green to dark purple. The hexafluoro-2-butyne and diethyl ether were removed and the ampoule brought back into the dry box, where the residue was extracted by toluene. The solution was concentrated and cooled to -30°C to yield dark purple crystals of **3** (0.118g, 50%). ^{1}H NMR (C_6D_6): 8.07 (br), 7.55 (br), 6.70 (br), 6.60 (br), 6.00 (br), 4.90 (br), 3.80 (br), 3.26 (br), 2.76 (br), 1.88 (br), 1.50 (br), 1.28 (br), 1.15 (br), 0.90 (br), 0.40 (br), -0.27 (br), -0.46 (br) ppm. UV/Vis (toluene): λmax (ε) = 498 (2354 M^{-1} cm^{-1}), 626 (1422 M^{-1} cm^{-1}), 751 (741 M^{-1} cm^{-1}). **3** is too thermally unstable to attempt characterization by elemental analysis.[a]

X-ray structural analysis for **2a**, **2b**, **2b•**(diethylether), **2c•**(toluene), and **3•**2.5(toluene): crystal data and refinement details are summarized in Table 1S. A diethylether solvated crystal phase of **2b** is also included in the CIF deposition. Crystals were selected and mounted on plastic mesh using viscous oil flash-cooled to the data collection temperature. Data were collected on a Brüker-AXS APEX CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ=0.71073 Å). Unit cell parameters were obtained from 60 data frames, 0.3º ω, from three different sections of the Ewald sphere. The systematic absences in the data and the unit cell parameters were consistent to *C*2/*c* and *Cc* for **3•**2.5(toluene); and, uniquely, for $P2_1/n$ [=$P2_1/c$] for the others. The centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement for **3•**2.5(toluene). The data-sets were treated with SADABS absorption corrections based on redundant multiscan data.[1] The structures were solved using direct methods and refined with full-matrix, least-squares procedures on F^2. Molecules of solvation for **2c•**(toluene), and **3•**2.5(toluene) were treated as diffused contributions (Squeeze, Platon).[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Atomic scattering factors are contained in the SHELXTL 6.12 program library (Sheldrick, G. M., *op. cit*.). The CIFs are deposited with the CSD under CCDC 839343 – 839347.

[a] The thermal stabilities of the alkyne complexes decrease in the order **2a** > **2b** > **2c** > **3**; deviations in the elemental analyses are likely due to partial sample decomposition during shipping.

Table 1S. Crystallographic data for complexes **2a-c** and **3**

	2a	**2b**	**2c**·toluene	**3**·2.5toluene
Formula	$C_{56}H_{78}Cr_2N_4$	$C_{58}H_{82}Cr_2N_4$	$C_{73}H_{90}Cr_2N_4$	$C_{73.5}H_{92}Cr_2F_6N_4$
Fw	911.22	939.28	1127.49	1249.51
space group	P2(1)/n	P2(1)/n	P2(1)/n	C2/c
Color	purple	purple	purple	Purple
a, Å	13.627(3)	13.145(3)	18.399(4)	28.416(5)
b, Å	19.352(4)	23.048(6)	13.333(3)	23.911(4)
c, Å	20.122(4)	18.413(5)	27.223(6)	21.946(4)
α, deg	90	90	90	90
β, deg	100.097(4)	105.677(4)	106.668(4)	104.553(4)
γ, deg	90	90	90	90
V, Å^3	5224.3(17)	5371(2)	6397(3)	14433(5)
Z	4	4	4	8
D(calcd), g cm^{-3}	1.159	1.162	1.171	1.150
μ(Mo Kα), mm^{-1}	0.454	0.444	0.384	0.358
temp, K	200(2)	200(2)	200(2)	200(2)
no. data/params	13006 / 577	13376 / 595	15966 / 665	17963 / 629
GOF on F^2	1.004	1.038	1.018	1.014
R(F), [a]	0.0651	0.0641	0.0696	0.0594
$R_w(F^2)$, [a]	0.1368	0.1576	0.1532	0.1256

[a] Qantity minimized: $R_w(F^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |F_o - F_c|$.

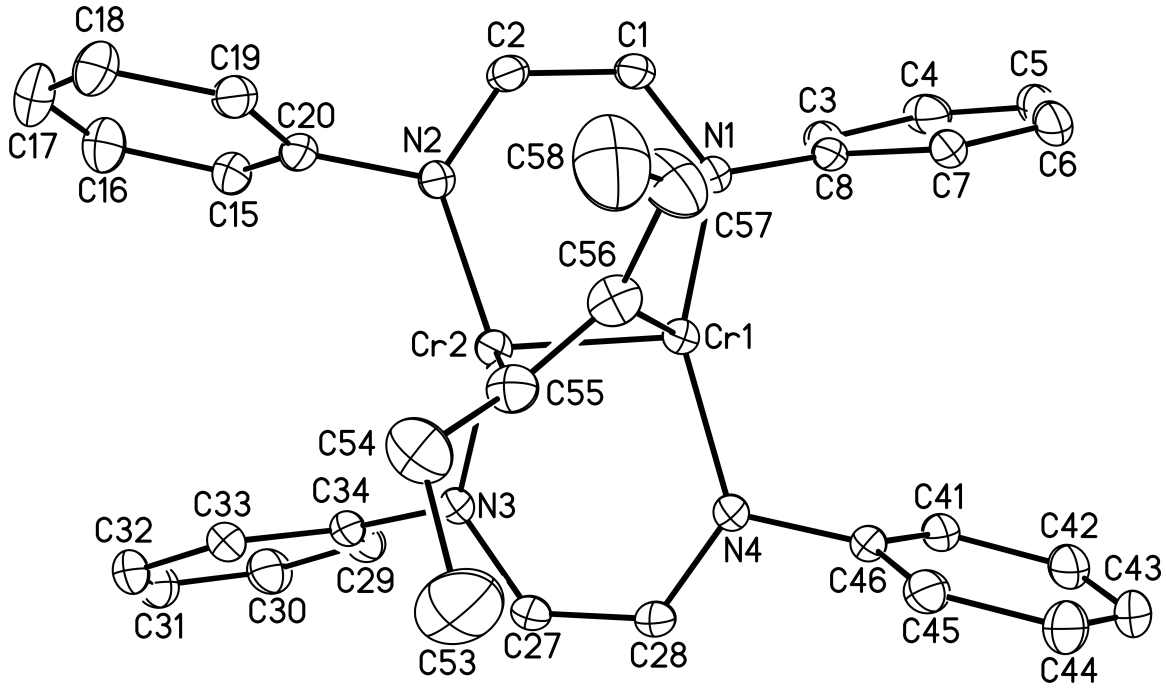

Fig. 1S The molecular structure of **2b** with thermal ellipsoids at the 30% probability level; H-atoms and ligand isopropyl groups have been omitted for clarity. Selected distances [Å] and angles [°]: Cr1–Cr2 1.9361(7), Cr1–N1 1.908(2), Cr1–N4 1.893(2), Cr2–N2 1.926(2), Cr2–N3 1.945(2), Cr1–C56 2.073(3), Cr2–C55 1.963(3), C55–C56 1.315(4), N1–C1 1.376(3), C1–C2 1.355(4), N2–C2 1.368(3), N3–C27 1.372(3), C27–C28 1.347(4), N4–C28 1.380(3), N1–Cr1–Cr2 106.16(6), N1–Cr1–N4 142.37(9), Cr2–Cr1–N4 102.66(6), N1–Cr1–C56 106.69(11), Cr2–Cr1–C56 66.97(9), N4–Cr1–C56 106.57(11), N2–Cr2–N3 126.13(9), N2–Cr2–Cr1 103.96(6), N3–Cr2–Cr1 103.39(6), N2–Cr2–C55 118.42(11), N3–Cr2–C55 108.12(11), Cr1–Cr2–C55 87.78(9).

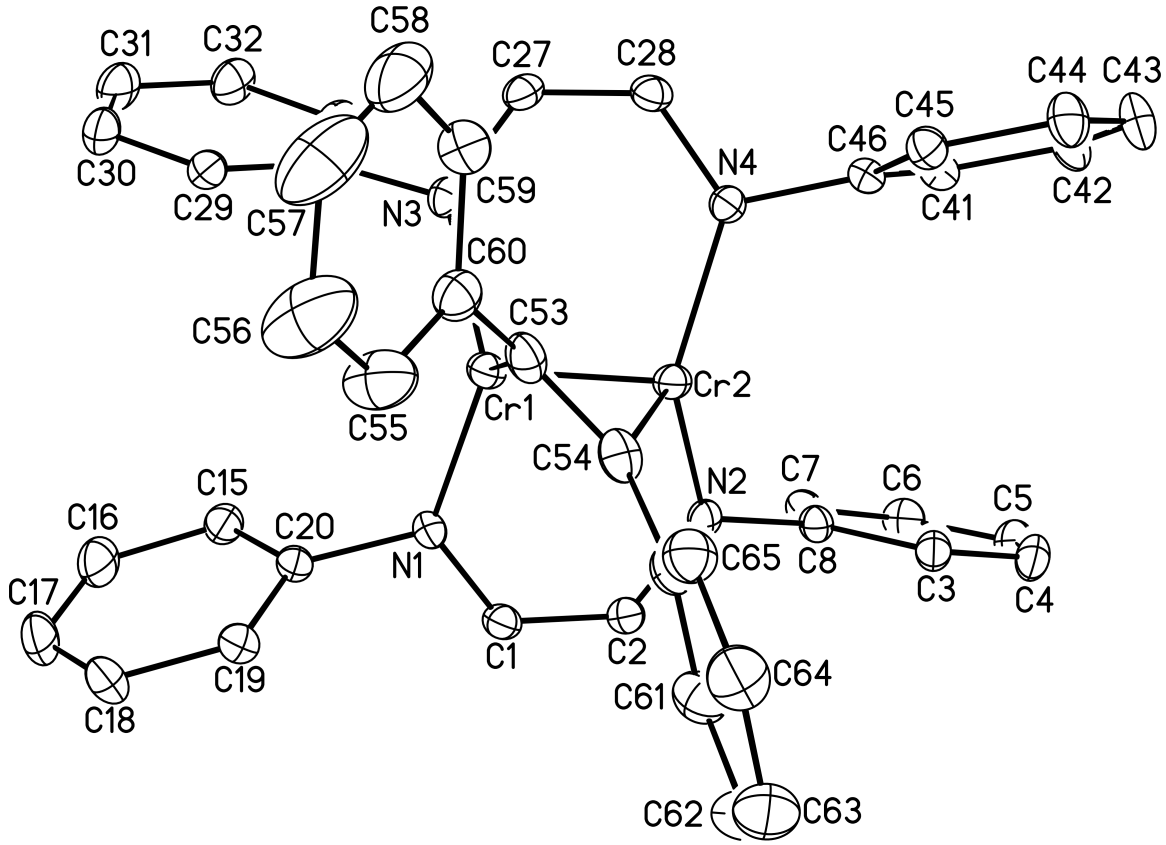

Fig. 2S The molecular structure of **2c**·toluene with thermal ellipsoids at the 30% probability level; H-atoms, solvent molecules and ligand isopropyl groups and toluene solvent molecule have been omitted for clarity. Selected distances [Å] and angles [^{o}]: Cr1–Cr2 1.9186(7), Cr1–N1 1.935(2), Cr1–N3 1.928(2), Cr2–N2 1.915(2), Cr2–N4 1.910(2), Cr1–C53 1.992(3), Cr2–C54 2.056(3), C53–C54 1.339(4), N1–C1 1.366(3), C1–C2 1.355(4), N2–C2 1.378(3), N3–C27 1.370(3), C27–C28 1.345(4), N4–C28 1.380(3), N1–Cr1–Cr2 104.06(7), N1–Cr1–N3 129.12(9), Cr2–Cr1–N3 105.56(7), N1–Cr1–C53 119.99(11), Cr2–Cr1–C53 81.04(8), N3–Cr1–C53 104.85(11), N2–Cr2–N4 134.28(9), N2–Cr2–Cr1 106.32(6), N4–Cr2–Cr1 103.51(6), N2–Cr2–C54 110.11(11), N4–Cr2–C54 111.55(10), Cr1–Cr2–C54 72.29(8).

Calculations. Geometry optimizations of the full structures were performed using gradient-corrected density-functional theory (DFT) in C_1 symmetry. Exchange and correlation were treated by a combination of Becke's exchange (B) and Lee, Yang and Parr's correlation (LYP) functional (BLYP).[3-5] A self-consistent-field (SCF) convergence criterion of 10^{-6} hartree and the standard grid (*m*3) for numerical quadrature were used.[6] Basis sets of double-zeta quality with polarization functions on all atoms (def2-SVP)[7] were used for all atoms except for the metal where we used basis sets of triple-zeta quality with polarization functions for the valence electrons (LANL08(f)) and treated the core electrons by an effective core potential (LANL2DZ ECP). For structure optimizations all energy and gradient calculations were carried out using the TURBOMOLE V5.10 suite of programs [8] within the multipole accelerated RI-J approximation (MARI-J).[9] The geometry optimizations were driven by Gaussian 03 using the Berny algorithm employing redundant internal coordinates and standard convergence criteria.[10] Initially the functionals BP86, PBE, BLYP, TPSS, B3LYP, PBE0, VSXC, tHCTH, B3PW91 were considered and their performances in reproducing the crystallographic structure of **1** were compared. BLYP was selected for giving closest agreement with the experimental data. All reported structural parameters refer to singlet ground state structures.

For NBO/NPA analysis single point calculations with the same basis sets, ECPs and functional were performed with the ORCA 2.7.0 program to generate gennbo input files. These were processed with the gennbo program (version 5.0).

Single point energy calculations employing full electron basis sets of triple-z quality with polarization functions for all atoms (def2-TZVP) were done with the ORCA 2.7.0 program.[11] The resolution of identity (RI) approximation as well as the chain of spheres approximation (RIJCOSX) were used.

References

1. G. M. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112-122.
2. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.
3. J. P. Perdew, *Physical Review B*, 1986, **33**, 8822-8824.
4. J. P. Perdew, *Physical Review B*, 1986, **34**, 7406-7406.
5. A. D. Becke, *Physical Review A*, 1988, **38**, 3098-3100.
6. O. Treutler and R. Ahlrichs, *J. Chem. Phys.*, 1995, **102**, 346-354.
7. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
8. TURBOMOLE V5.10 2008, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
9. M. Sierka, A. Hogekamp and R. Ahlrichs, *J. Chem. Phys.*, 2003, **118**, 9136-9148.
10. Gaussian 03, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.;

Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

11. Neese, F. ORCA - an ab initio, Density Functional and Semiempirical program package, Version 2.6. University of Bonn, 2008.