Supporting Information For:

High-Spin Supramolecular Pair of Mn(II)/Thiazyl Radical Complexes

Elisabeth M. Fatila,[a] Jordan Goodreid,[a] Rodolphe Clérac,[b,c] Michael Jennings,[d] Jalil Assoud[e] and Kathryn E. Preuss[a]*

Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1. CNRS, UPR 8641, Centre de Recherche Paul Pascal (CRPP), Equipe "Matériaux Moléculares Magnétiques", 115 avenue du Dr. Albert Schweitzer, Pessac, F-33600, France. Université de Bordeaux, UPR 8641, Pessac, F-33600, France. Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7. Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

Experimental Section

General Considerations. All reactions were performed under argon atmosphere with strict exclusion of air and water, using standard Schlenk and glove box techniques. Solvents were rigorously dried and distilled under argon prior to use; toluene was dried over sodium metal, THF over sodium/benzophenone ketyl, and acetonitrile over P_2O_5. All reagents were purchased from Aldrich and used as received, with the following exceptions: chlorotrimethylsilane was dried over CaH_2 prior to use; the diethyl ether adduct of lithium bis(trimethylsilyl)amide ($LiN(TMS)_2 \cdot Et_2O$) was prepared following literature procedure;[i,ii] manganese (II) bis(hexafluoroacetylacetonate) dihydrate ($Mn(hfac)_2 \cdot 2H_2O$) was prepared following literature procedure[iii] and was converted to the bis(THF) adduct by dissolution in dry, warm THF in the presence of Na_2SO_4. The drying agent was removed by filtration and the solvent was removed *in vacuo* to yield $Mn(hfac)_2 \cdot 2THF$; absence of OH peak at 3484 cm^{-1} in IR (KBr). NMR spectra were recorded on a Brüker Avance-400 spectrometer at 298 K. IR spectra were collected using a Nicolet 510-FTIR spectrometer at ambient temperature. Elemental analyses were performed by MHW Laboratories in Phoenix, Arizona.

Synthesis of 2-Benzoxazolecarbonitrile (boaCN): 2-Benzoxazolecarbonitrile (**boaCN**) was prepared in three steps starting with the synthesis of Appel's salt according to literature procedures.[iv,v] Reaction of Appel's salt with 2-aminophenol afforded the chloride salt of 2-[(4-chloro-5H-1,2,3-dithiazol-5-ylidene)aminophenol[v,vi,vii] which was reacted with four equivalents of pyridine and refluxed in toluene for 24 hours to obtain crude **boaCN**. The crude **boaCN** material was purified by extraction with CH_2Cl_2 followed by column chromatography (10:90, EtOAc:hexanes) to yield **boaCN** in 60% yield (as calculated from the chloride salt of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)aminophenol). Crystals of **boaCN** were obtained from slow evaporation of the column chromatography eluent and were suitable for X-ray crystallography. Literature procedures[v,vi,vii] use microwave heating to obtain **boaCN** from 2-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)aminophenol with a yield of 69% (as calculated from the free base).[vi]

Synthesis of Benzoxazole-*N*,*N*,*N′*-tris(trimethylsilyl)amidine (BOADS): A solution of **boaCN** (0.9617 g, 6.674 mmol) in 5 mL of toluene was added drop-wise to a stirring solution of $LiN(TMS)_2 \cdot Et_2O$ (1.7785 g, 7.3659 mmol) in 40 mL of toluene. The dark red solution was stirred for 2.5 h. A solution of chlorotrimethylsilane (1.3 mL, 10 mmol) in 5 mL of toluene was then added drop-wise and the resulting red solution was stirred for 12 hours. The crude product was filtered *in vacuo* to afford a pale red-orange viscous liquid and was used without any further purification. ^{1}H NMR data was obtained to confirm the presence of **BOADS**. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.79 (m, 1H), 7.77 (m, 1H), 7.62 (m, 1H), 7.60 (m, 1H), 0.15 (s, 27 H). IR (NaCl-neat): 2955(m), 2899(mw), 1643(ms), 1605(ms), 1541(m), 1410(m), 1341(mw), 1294(m), 1251(s), 1140(m), 1105(m), 1006(ms), 933(m), 881(ms), 844(s), 752(ms), 654(mw), 624(w), 594(w), 492(w), 465(mw) cm^{-1}.

Synthesis of 4-(Benzoxazol-2'-yl)-1,2,3,5-Dithiadiazolium chloride, [1]Cl: A solution of crude **BOADS** (3.12 g, 8.26 mmol) in 10 mL acetonitrile was added slowly to a stirring solution of excess sulfur monochloride (4.0 mL, 50 mmol) in 50 mL of acetonitrile. The black slurry was stirred for 12 hours at room temperature under argon to afford crude **[1]Cl** as a black solid, which was washed once with 20 mL of room temperature acetonitrile, filtered and dried *in vacuo*. The crude **[1]Cl** was used without any further purification. IR (KBr): 3097(s), 3012(s), 1693(m), 1610(m), 1561(m), 1522(mw), 1473(m), 1448(m), 1417(s), 1336(s), 1264(mw), 1232(m), 1164(s), 1107(m), 1006(mw), 983(mw), 893(w), 878(s), 841(s), 776(m), 736(m), 648(m), 623(mw), 556(mw), 513(w), 436(w) cm^{-1}.

Synthesis of 4-(Benzoxazol-2'-yl)-1,2,3,5-Dithiadiazolyl (boaDTDA) 1: Triphenylantimony (2.76 g, 7.82 mmol) was added using a powder funnel to a slurry of **[1]Cl** (2.71 g, 10.5 mmol) in 20 mL of acetonitrile. The dark purple solution was stirred for 1 h at room temperature and then filtered to afford a dark purple precipitate that was dried *in vacuo*. Dynamic vacuum sublimation (10^{-2} torr) at 90 ºC using a gradient-temperature tube furnace, afforded dark purple blocks of **1** which were also suitable for X-ray crystallography; yield 0.619 g (41.7% yield from nitrile). IR (KBr): 3075(s), 1606(m), 1558(m), 1475(m), 1448(ms), 1388(ms), 1333(m), 1305(ms), 1285(mw), 1243(mw), 1222(ms), 1187(mw), 1161(s), 1108(m), 1003(mw), 976(w), 969(mw), 934(w), 901(w), 887(w), 833(ms), 805(m), 785(ms), 771(s), 759(ms), 739(s), 724(m), 624(w), 618(w), 609(w), 528(w), 495(w), 489(w), 428(mw) cm^{-1}. Anal. Calcd for $C_8H_4N_3OS_2$: C, 43.23; H, 1.81; N, 18.91%. Found: C, 43.40; H, 1.75; N, 19.16%. EPR (CH_2Cl_2, 25°C) 1:2:3:2:1 five line pattern consistent with coupling to two equivalent ^{14}N nuclei; $g = 2.010(4)$, $a_N = 5.047$ G.

Synthesis of (boaDTDA)Mn(hfac)$_2$ 2: Crystalline **1** (0.1619 g, 0.7270 mmol) was dissolved slowly in 115 mL of warm CH_2Cl_2 to which $Mn(hfac)_2{\cdot}2THF$ (0.4623 g, 0.7539) was added. The very dark blue-green solution was stirred for 1h and the solvent was removed to afford **2** as a dark purple solid that was dried *in vacuo*. Dynamic vacuum sublimation (10^{-2} torr) at 110 ºC using a gradient-temperature tube furnace, afforded green-black rectangular blocks of **2** suitable for X-ray crystallography and magnetic study, yield 0.1168 g (23%). IR (KBr): 3297(vw), 3138(vw), 3106(vw), 1647(s), 1618(mw), 1599(mw), 1558(m), 1531(m), 1496(ms), 1449(m), 1435(m), 1347(m), 1318(mw), 1257(s), 1200(s), 1146(s), 1105(m), 1097(m), 948(w), 922(w), 883(w), 853(mw), 800(ms), 782(mw), 760(m), 748(m), 733(mw), 666(ms), 629(w), 615(w), 585(m), 544(w), 527(w), 499(w), 478(vw), 428(w) cm^{-1}. Anal. Calcd for $Mn(C_5HO_2F_6)_2(C_8H_4N_3OS_2)$: C, 31.27; H, 0.87; N, 6.08%. Found: C, 31.04; H, 0.97; N, 6.03%.

Cyclic Voltammetry (CV): Electrochemical measurements were performed on an Autolab PGSTAT30 using a three-electrode glass cell sealed under an argon atmosphere. The working, reference and counter electrodes were all platinum wire; electrodes were carefully washed with toluene followed by hydrogen flame and subsequently cleaned with ethanol and dried prior to use. Measurements were referenced *in situ* against the ferrocene/ferrocenium couple ($E_{1/2}$ (ox) = 0.46 V in methylene chloride with [nBu$_4$N][PF$_6$] as supporting electrolyte)[viii] and are reported versus SCE. The CV of **1** (2.3 mM) in dry, degassed CH_2Cl_2 (0.1 M [nBu$_4$N][PF$_6$]) shows a chemically reversible oxidation at $E_{1/2}$ (ox) = 0.99 V (peak-to-peak potential difference ΔE_{pp}= 200 mV) and an irreversible reduction at a cathodic peak potential E_{pc} = -0.82 V.

Electron Paramagnetic Resonance Spectroscopy: EPR spectra were obtained using a Brüker EMX spectrometer. In CH_2Cl_2 (RT), **1** exhibits a 1:2:3:2:1 5-line pattern corresponding to coupling of an unpaired electron with two equivalent ^{14}N nuclei (a_N = 5.047 G, g = 2.010(4)).

Crystallographic Measurements. For 2-cyanobenzoxazole, data were collected at low temperature (150 K) with a Bruker APEX2 area detector diffractometer using APEX2 software, with Mo Kα radiation (λ = 0.71073 Å). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using Bruker SAINT. The absorption correction was applied using SADABS. The SHELX-TL V6.1 (Sheldrick, G.M.) program package was used to solve (using Direct Methods) and refine the structure using successive difference Fouriers. All hydrogen atoms were calculated geometrically as riding on their respective carbon atoms. The structure was disordered with respect to the benzoxazole O and N atom positions. They were modeled isotropically in an equal ratio, with soft restraints applied to keep the ADP's identical for the overlapping N/O atoms. Further, the bond lengths were allowed to refine but restrained to be identical for C-N and C-O first-order bonding. Specific crystal data details of the structures can be found in the CIF files.

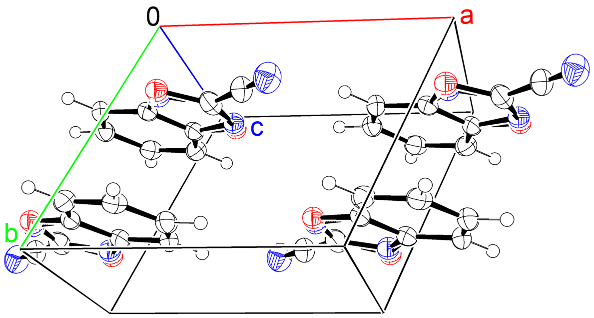

Figure S1. Crystal structure of 2-cyanobenzoxazole (displacement ellipsoids at 50%; H atoms omitted) shows disordered packing with respect to the benzoxazole O and N atom positions.

A dark purple block of 4-(benzoxazol-2'-yl)-1,2,3,5-dithiadiazolyl (boaDTDA) **1** was immersed in paratone oil and collected at low temperature (173 K) on a Brüker D8 three circle diffractometer with a SMART 6000 area detector using Cu Kα radiation (λ= 1.5418 Å) from a rotating Rigaku anode source. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using Brüker SAINT. The absorption correction was carried out using SADABS. The SHELX-TL V6.1 (Sheldrick, G.M.) program package was used to solve the structure by Direct Methods. Subsequent difference

Fourier syntheses allowed the remaining atoms to be located. Four independent molecules were formed and were very well ordered. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. The largest residue electron density peak (0.41 e/Å^3) was associated with one of the sulfur atoms. Full-matrix least squares refinement on F2 gave R1 = 3.91 for 4 sigma data and wR2 = 10.83 for all data (GOOF = 1.049).

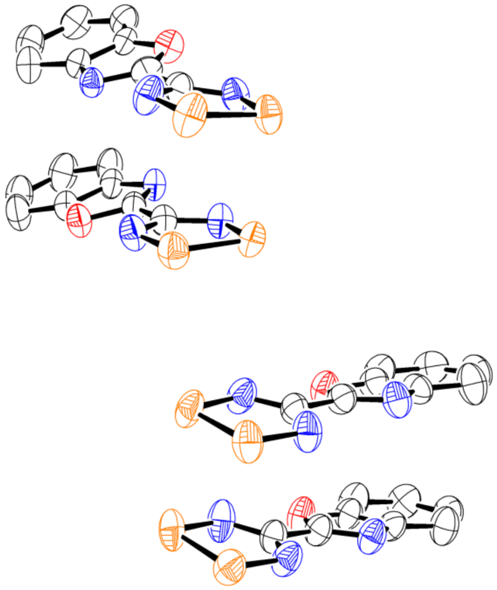

Figure S2. The crystal structure ligand **1** (boaDTDA) reveals two *cis*-cofacial dimers in the asymmetric unit. In one dimer, the benzoxazole rings are oriented such that like heteroatoms are superimposed, and in the other the benzoxazole nitrogen and oxygen atoms are superimposed.

A dark green block-shaped single crystal of (boaDTDA)Mn(hfac)$_2$ **2** was immersed in FOMBLIN Y oil (HVAC 140/13, Sigma-Aldrich), mounted on a glass fiber and collected on a Bruker AXS SMART-CCD equipped with an area detector utilizing graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and a Cryostream N$_2$ cooling device (Oxford cryosystem) at 200 K. The data collection was performed by scans of 0.3° in ω in four groups of 600 frames at 0°, 90°, 180° and 270° with an exposure time of 30 seconds. The data were corrected for Lorentz and polarization effects. Absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements using the APEX II package. The space group was determined on the basis of the systematic absences and it points toward the space groups $P2_1$ or $P2_1/m$ with (E^2-1) = 0.815 using the APEX II package. Structure solution using direct method and Patterson method (SHELXTL of APEX II package) in the space group $P2_1/m$ failed and it was successful in the chiral space group $P2_1$ using direct method. The refinement on the F^2 using the least square method resulted in the R and wR values of 0.0515 and 0.1340 (all data) respectively. The structure contains two crystallographically independent molecules noted (boaDTDA)Mn1(hfac)$_2$ and (boaDTDA)Mn2(hfac)$_2$. The command ADDSYM component of the PLATON program was used to check for additional symmetry and it confirmed the choice of space group $P2_1$.

Magnetic Measurements. Magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. The samples were prepared in a glove box under argon and sealed in a plastic bag in order to avoid any contact with oxygen or moisture. For **1**, the solid state sample was confirmed to be diamagnetic as expected for π-dimers of DTDAs. For **2**, ac susceptibility measurements were measured with an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz, but no out-of-phase ac signal was detected. The magnetic data were corrected for the sample holder and the diamagnetic contribution.

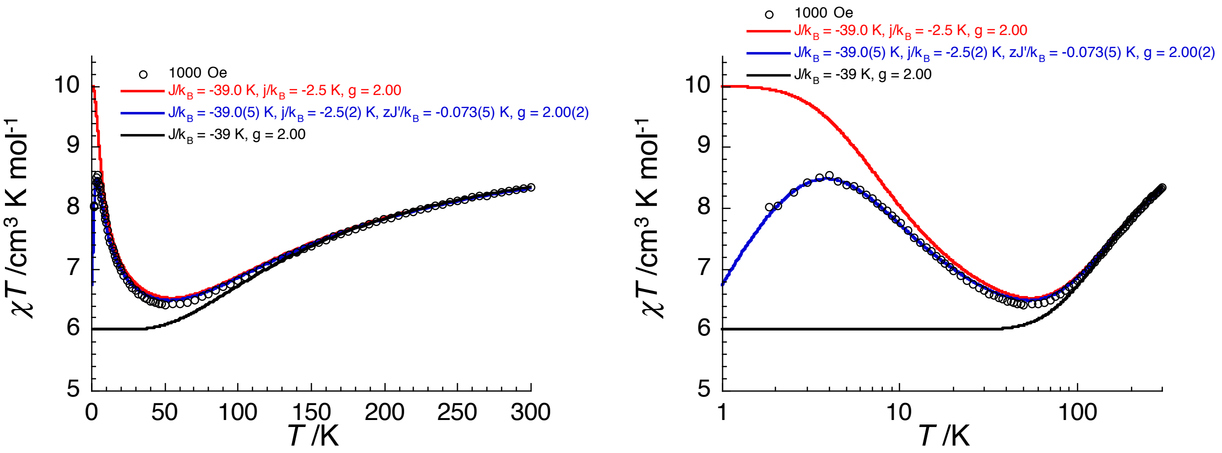

Figure S3. Linear (left) and semi-logarithm (right; in order to better illustrate the quality of the simulation to the data at low temperature) plots of χT versus T for complex **2**, collected at 1000 Oe (with χ being the molar susceptibility defined as M/H normalized per [Mn(hfac)$_2$(boaDTDA)]$_2$ pair). The best simulation of the data is shown in blue taking into account the g factor, the intra-molecular and intra-pair magnetic interactions, J and j respectively (see Figure 2), and the inter-pairs magnetic coupling (J') treated in the mean field approximation (see text). In black and red lines are shown the calculated χT product versus T keeping respectively only the (g, J) and (g, J, j') parameter values from the simulation display in blue.

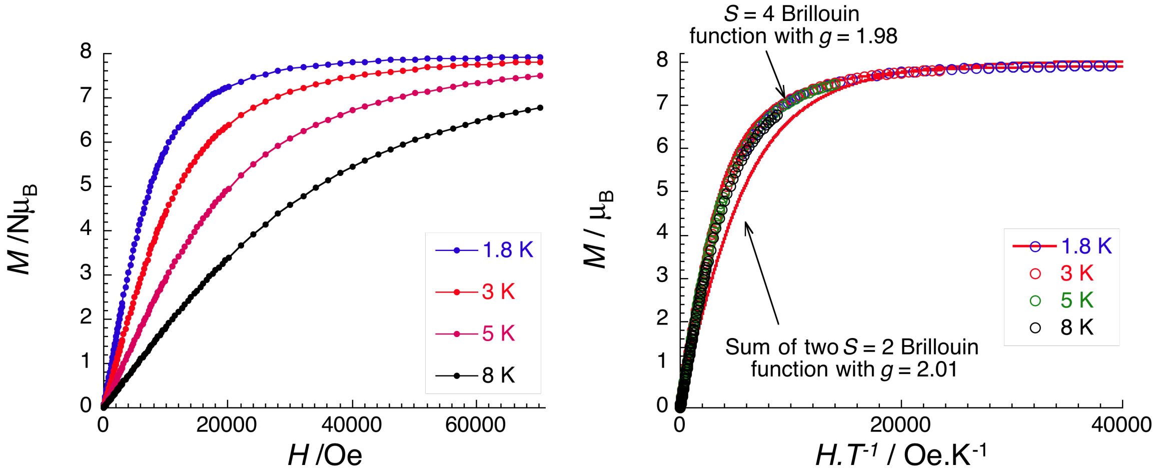

Figure S4. (Left) Field dependence of the magnetization of **2** below 8 K (normalized per $[Mn(hfac)_2(boaDTDA)]_2$ pair) with a saturation at 7.92 μ_B under 7 T (1.8 K) as expected for an $S_T = 4$ ground state for a pair of $Mn(hfac)_2(boaDTDA)$ units ($g \approx 2$). (Right) M versus H/T plots below 8 K for **2**. As indicated on the plot, the solid lines correspond to the fits of the experimental data to a sum of two $S = 2$ Brillouin functions and to an $S = 4$ Brillouin function. This plot emphasizes that the best fit is obtained with an $S = 4$ Brillouin function that confirms the nature of the $S_T = 4$ ground state for a pair of $Mn(hfac)_2(boaDTDA)$ units.

Computational Study. A single point energy calculation using the crystal geometry of the "Mn1"-containing molecule and specifying an $S = 2$ ground state was performed using Gaussian03 for Windows[ix] (ub3lyp/6-31G* and SDD extra basis set for Mn). Spin density and molecular orbital pictures were generated using Gauss View 3.0 (surface isovalue 0.02) (Figure S5). The occupied alpha frontier molecular orbitals are primarily metal-centered with significant distribution onto the hfac oxygen atoms. The highest occupied beta molecular orbital is primarily the π* orbital of the DTDA ring, distributed over the sulfur and nitrogen atoms. This is in good agreement with a spin model of the molecule as one unpaired electron on the boaDTDA ligand AF coupled to five unpaired electrons on the $Mn(hfac)_2$ fragment. Considering the geometry of a supramolecular pair, the shape of the frontier molecular orbitals is in keeping with a non-orthogonal overlap between alpha frontier molecular orbitals (on the hfac oxygen atoms) of one molecule and the highest occupied beta molecular orbital (on the sulfur atoms) of the other molecule. This supports the proposed mechanism whereby AF coupling between the ligand-based spin of one molecule and the metal-based spin of the other molecule generates an $S = 4$ ground state for a pair.

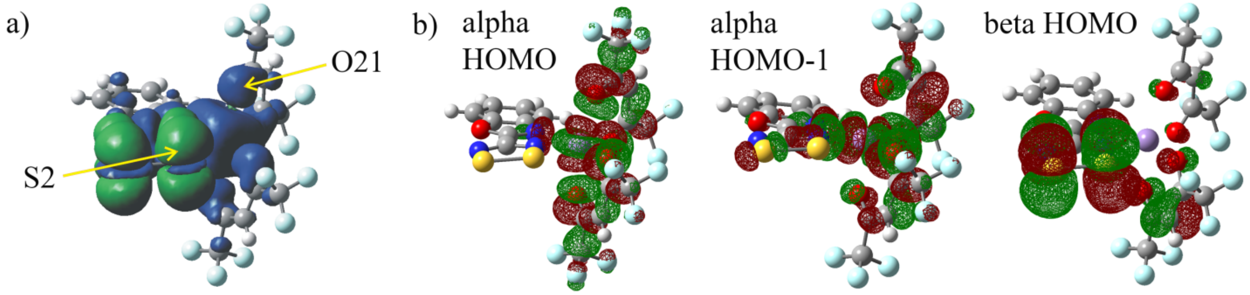

Figure S5. (a) A plot of the calculated spin density for **2** (crystal structure geometry of the "Mn1"-containing molecule shown) reveals positive spin density (blue) on the O21 atom and negative spin density (green) on the S2 atom. (b) Representative frontier alpha MOs show "lobes" on O21 and the highest occupied beta MO is a π* DTDA centered orbital.

---

[i] Boeré, R.T.; Oakley, R.T.; Reed, R.W. *J. Organomet. Chem.* **1987**, *331*, 161.

[ii] Wannagat, U.; Niederprüm, H. *Chem. Ber.* **1961**, *94*, 1540.

[iii] Izumi, F.; Kurosawa, R.; Kawamoto, H.; Akaiwa, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*(11), 3188.

[iv] Appel, R.; Janssen, H.; Siray, M.; Knoch, F. *Chem. Ber.* **1985**, 118, 1632.

[v] English, R.F.; Rakitin, O.A.; Rees, C.W.; Vlasova, O.G. *J. Chem. Soc. Perkin Trans. 1* **1997**, 201.

[vi] Frère, S.; Thiéry, V.; Bailly, C.; Besson, T. *Tetrahedron* **2003**, 59, 773.

[vii] Rees, C.W. *J. Heterocyclic Chem.* **1992**, 29, 639.

[viii] Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

[ix] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennuci, 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.; 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.; 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.; Pople, J. A. *Gaussian 03*, Revision B.03; Gaussian, Inc. Pittsburgh, PA, 2003.