Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2014

Electronic Supporting Information

CO_2 and SO_2 Activation by a Cr-Cr Quintuple Bond

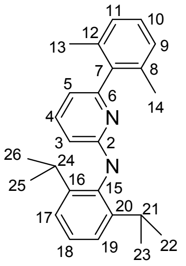
Awal Noor,[a] Sadaf Qayyum, [a] Tobias Bauer, [a] Stefan Schwarz, [a] Birgit Weber [a] and Rhett Kempe [a] *

[a] Lehrstuhl Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth (Germany). E-mail: Kempe@uni-bayreuth.de

Synthese of the metal complexes

General Procedures

All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in N_2 filled glove box (mBraun 120-G) with a high-capacity recirculator (<0.1ppm O_2). Solvents were dried by distillation from sodium wire/benzophenone. Complex **1** was prepared according to published procedure.[1] Commercial $CrCl_2$ (Alfa Aesor) was used as received. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. NMR spectra were recorded on Brucker 250 MHz, Varian 300 MHz and Varian 400 MHz at ambient temperature and the IR data were recorded on Jasco FT/IR–6100. The chemical shifts are reported in ppm relative to the internal TMS. Elemental analyses (CHN) were determined using a Vario EL III instrument. X-ray crystal structure analyses were performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97,[2] SHELXL97[3] and WinGX.[4] CCDC-1009949 (**2**), 1009951 (**3**) and 1009950 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).



Synthesis of 2: Method 1: 1 (0.082 g, 1 mmol) was dissolved in toluene (15 mL) and degassed before CO_2 (0.2 bar) was introduced into it, at room temperature. A colour change from purple to brown green was observed within 10 minutes. The reaction mixture was further stirred for two hours and then kept t -25 °C under CO_2 atmosphere to afford brown crystals of **2**. Isolated yield: (26%). To determine the yield of **2** in solution, CO_2 was introduced into **1** (41 mg) in C_6D_6 (0.3 mL) and the integration of the diamagneic specie was carried out with respect to the standard (≈ 60%). **Method 2:** CO (0.2 bar) was introduced into **1** (0.4 g, 0.48 mmol) in toluene (10 mL) at room temperature with continuous stirring. A colour change from purple to brown was observed within 10 minutes. The mixture was stirred under CO atmosphere for about three hours. The solution was filtered and the filtrate was kept at -30°C to afford brown crystal. Yield: 0.076g (18.09%). $C_{52}H_{58}Cr_2N_4O_2.C_7H_8$ (966.4): Calc. C 73.27 H 6.88 N 5.79; Found. C 73.03 H 6.46 N 5.46. IR (Fomblin YR-1800, 26°C, cm^{-1}): 1924 υ(C=O), 1806 υ(C=O). IR (Toluene, 26°C, cm^{-1}): 1942 υ(C=O), 1857 υ(C=O). ^1H NMR (300 MHz, C_6D_6): δ =1.06 (d, 12H, J = 6.8 Hz, $H^{22,23,25,26}$), 1.36 (d, 12H, J = 6.8 Hz, $H^{22,23,25,26}$), 2.11 (s, 6H, $H^{13,14}$), 3.13 (sep, 4H, J = 6.8 Hz , $H^{21,24}$), 5.79 (d, 2H, J = 5.9 Hz, H^3), 5.95 (d, 2H, J = 8.9 Hz , H^5), 6.44 (tr, 2H, J = 7.3 Hz, H^4), 6.63 (d, 4H, J = 7.5 Hz, $H^{17,19}$), 6.67 (d, 4H, J = 6.8 Hz, $H^{9,11}$), 6.98-7.21 (m, 4H, $H^{10,18}$) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 19.6 ($C^{13,14}$), 24.6 ($C^{22,23,25,26}$), 25.0 ($C^{22,23,25,26}$), 28.7 ($C^{21,24}$), 107.1 (C^3), 109.9 (C^5), 123.9 ($C^{9,11}$), 127.8 ($C^{17,19}$), 128.5 (C^{18}), 128.8 (C^{15}), 134.5 (C^{10}), 135,6 ($C^{8,12}$), 136.9 (C^4), 141.9 (C^7), 145.4 ($C^{16,20}$), 155.6 (C^6), 164.5 (C^2), 291.6 (C^{CO}) ppm.

Synthesis of 3: **1** (0.082 g, 1 mmol) was dissolved in toluene (15mL) and degassed before N_2O was introduced into it, at room temperature. A quick colour change to brown was observed. It was stirred for half an hour and then cooled to -25 °C under N_2O atmosphere to give brown green needle like crystals of **7**. Yield: 0.072g (76%). $C_{100}H_{116}Cr_4N_8O_4$, (C_7H_8) (1794.17): Calc. C 71.63 H 6.97 N 6.25; Found. C 71.35 H 6.83 N 6.38.

Synthesis of 4: **1** (0.070 g, 0.85 mmol) was dissolved in a mixture of toluene (5mL) and hexane (15 mL) and degassed before SO_2 was introduced into it, at room temperature. Imidiate colour change from purple to orange was observed. It was stirred for half an hour and then cooled to -25 °C under SO_2 atmosphere to give orange crystals of **4** overnight. Yield: 0.057g (71 %). $C_{50}H_{58}Cr_2N_4O_4S_2.C_7H_8$ (1039.28): Calc. C 65.87 H 6.40 N 5.39; Found. C 65.01 H 6.36 N 5.65. ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 0.83 (br, 6H, $H^{22,23/25,26}$), 1.20 (br, 6H, $H^{22,23/25,26}$), 1.22 (br, 6H, $H^{22,23/25,26}$), 1.55 (br s, 6H, $H^{22,23/25,26}$), 1.94 (br s, 12H, $H^{13,14}$), 3.07 (br sep, 2H, $H^{21,24}$), 3.96 (v br, 2H, $H^{21,24}$), 5.33 (br, 2H, H^3), 5.71 (br, 4H, $H^{9,11/17,19}$), 6.92-7.25 (m 10H, $H^{4,5,9,10,11,17,18,19}$), 7.51 (br, 2H, $H^{10/18}$) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 20.1 ($C^{13,14}$), 20.5 ($C^{13,14}$), 21.8 ($C^{22/23/25/26}$), 23.9 ($C^{22/23/25/26}$), 25.5

($C^{22,23,/25,26}$), 26.7 ($C^{22,23/25,26}$), 27.7 ($C^{21,24}$), 28.2 ($C^{21,24}$), 103.7 (C^{3}), 111.2 (C^{5}), 114.6 (C^{18}), 124.2 (C^{18}), 126.0 (C^{10}), 126.2 (C^{10}), 127.2 ($C^{17,19}$), 127.3 ($C^{17,19}$), 127.4 ($C^{9,11}$), 127.8 ($C^{9,11}$), 134.7 ($C^{8,12}$), 135.9 ($C^{8,12}$), 137.4 (C^{4}), 137.8 (C^{7}), 139.0 ($C^{16,20}$), 142.5 ($C^{16,20}$), 148.1 (C^{15}), 149.5 (C^{6}), 149.9 (C^{6}), 159.3 (C^{2}), 160.0 (C^{2}) ppm.

Susceptibility measurements: Magnetic susceptibility measurements were carried out with a

Quantum Design MPMS-XL SQUID magnetometer in the range from 2 to 300 K. The powdered sample **3** was placed in a gelatin capsule, fixed in a nonmagnetic sample holder and measured in the RSO mode. The magnetic data were corrected for the diamagnetic contribution of the sample holder and gelatin capsule, respectively.

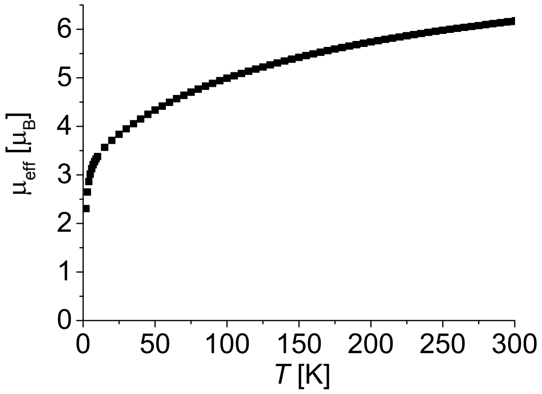


Figure S1: The temperature dependence of the molar magnetic susceptibility of **3**.

Computational Details:

Density functional theory (DFT) calculations were performed with the *TURBOMOLE* [1] program package. The RI-DFT method[5] applying the B-P86 functional[6] with the default grid was used for all calculations. The initial structure was obtained from the X-ray crystal structure. First optimization of the geometry was performed with the split-valence basis set def2-SV(P)[7] for all atoms. The obtained geometry was optimized a second time applying the triple zeta basis set def2-TZVP.[8]

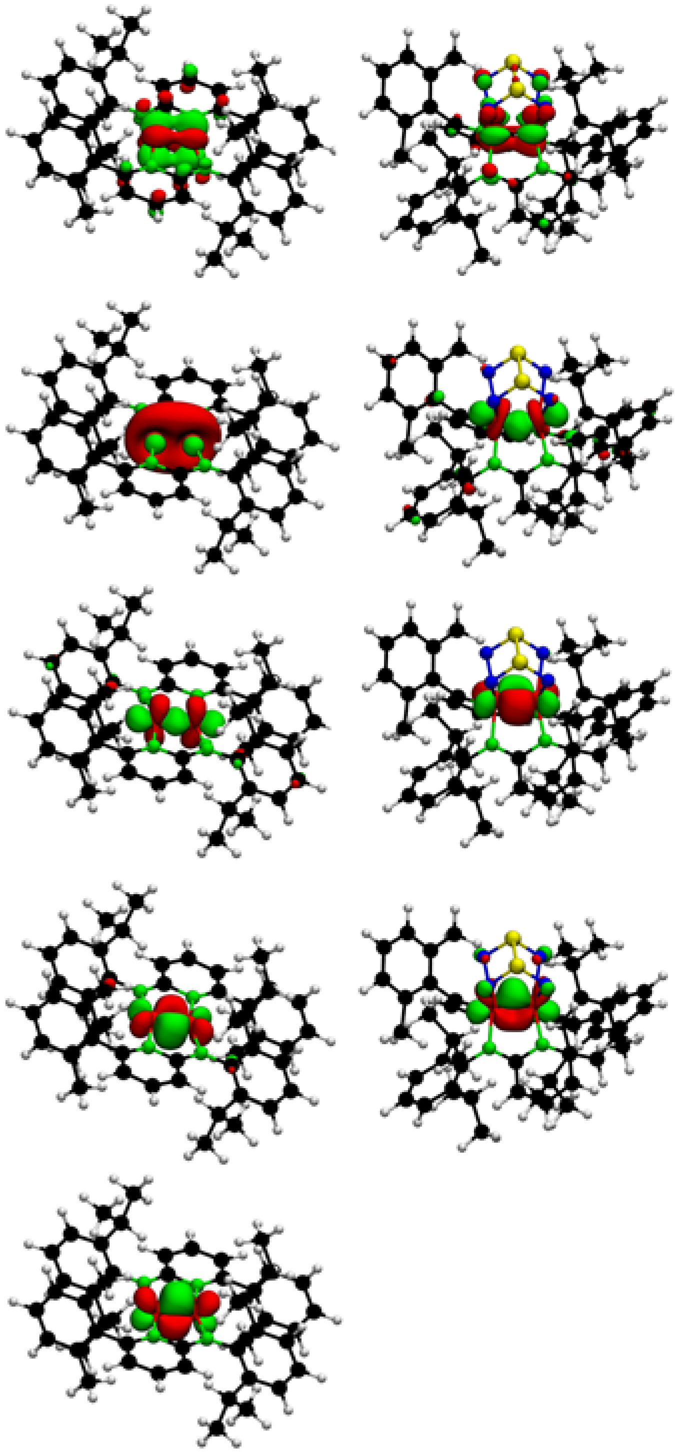


Figure S2: Frontier orbitals of **1** (left, from top to bottom: HOMO, HOMO-1, HOMO-4, HOMO-9, HOMO-12), **4** (right, from top to bottom: HOMO, HOMO-12, HOMO-13, HOMO-14). Orbital energies are given in Table S1.

Table S1: Energies (in E_h).of the d-type Cr-Cr-bonding orbitals of **1** and **4**.

1			**4**		
Orbital	AOs	Energy	Orbital	AOs	Energy
HOMO	d_{xz}	-0.14560	HOMO	d_{xz}	-0.15340
HOMO-1	d_{z^2}	-0.14972	-	-	-
HOMO-4	$d_{x^2y^2}$	-0.19657	HOMO-12	d_{z^2}	-0.22826
HOMO-9	d_{yz}	-0.21756	HOMO-13	d_{xy}	-0.23366
HOMO-12	d_{xy}	-0.22481	HOMO-14	d_{yz}	-0.23823

Table S1. Bond lengths, bond angles and relative energies for the experimental and calculated structures **1** and **4**.

Compound	Cr-Cr [Å]	Cr-O [Å]	S-S [Å]	N-Cr-N [°]	E [kcal mol^{-1}]
1 (calculated)	1.670	-	-	162.0	0
1 (X-ray)	1.750	-	-	165.0	-
4 (calculated)	1.789	2.082	2.465	101.1	-55.32
4 (X-ray)	2.342	2.062	2.379	98.2	-

Table S2. Formal charges derived from population analysis based on occupation numbers (PABOON).[8]

Atom	**1**	**4**	SO_2
Cr	0.09	-0.24	-
S	-	0.79	1.11
O	-	-0.65	-0.56-

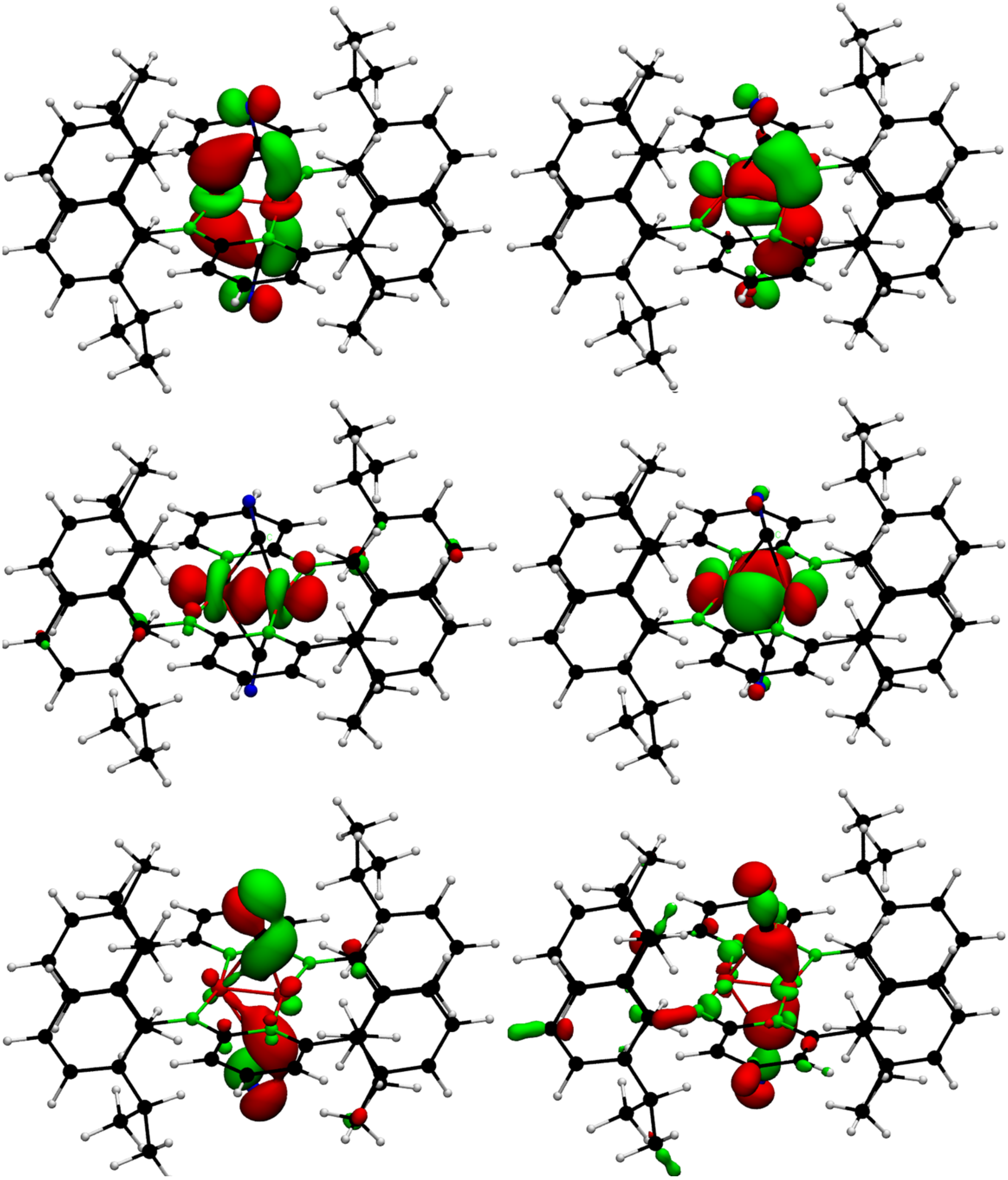


Figure S3: Molecular orbitals involved in the Cr-Cr and Cr-CO bond of **2**: HOMO (top, left), HOMO-2 (top, right), HOMO-5 (middle, left), HOMO-11 (middle, right), HOMO-54 (bottom, left), HOMO-70 (bottom, right).

Table S3. Bond length, bond angles and DFT energy for the experimental and calculated structure of **2**.

Compound	Cr-Cr [Å]	Cr1-C_{CO} [Å]	Cr2-C_{CO} [Å]	Cr2-Cr1-C_{CO} [°]	Energy [E_h]
2 (X-ray)	1.886	2.066	2.092	63.7	-4476.3803
2 (calculated)	1.818	1.961	2.231	72.2	-4476.3889

Table S4: Energies (in E_h).characterization of the orbitals in Figure S3.

Orbital	Energy	Description
HOMO	-0.14560	π-backbond Cr-CO
HOMO-2	-0.14972	π-backbond Cr-CO
HOMO-5	-0.19657	d_{z^2} Cr-Cr
HOMO-11	-0.21756	d_{yz} Cr-Cr
HOMO-54	-0.35124	σ-bond Cr-CO
HOMO-70	-0.37471	σ-bond Cr-CO

1 A. Noor, G. Glatz, R. Müler, M. Kaupp, S. Demeshko and R. Kempe, *Nature Chem.* 2009, ***1***, 322−325.

2 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, SIR 97: A new tool for crystal determination and refinement. *J. Appl. Cryst*. 1999, **32**, 115−119.

3 SHELX97 Programs for crystal structure analysis (Release 97-2). (G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998).

4 L. J. Farrugia, WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Cryst*. 1999, **32**, 837−838.

5 a) K. Eichkorn, O. Treutler, H. Öhm, M. Haser and R. Ahlrichs, *Chem. Phys. Letters* 1995, **242**, 652−660; b) K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor.*

Chem. Acc. 1997, **97**, 119−124; c) M. Sierka, A. Hogekamp and R. Ahlrichs; *J. Chem. Phys*. 2003, **118**, 9136−9148.

6 a) P. A. M. Dirac, *Proc. Royal Soc. (London) A* 1929, **123**, 714–733; b) J. C. Slater, *Phys. Rev.* **1951**, *81*, 385–390; c) S. Vosko, L. Wilk and M. Nussair, *Can. J. Phys.* 1980, **58**, 1200–1211; d) A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098–3100; e) P. Perdew, *Phys. Rev. B* 1986, **33**, 8822–8824.

7 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.,* 2005, **7**, 3297–3305.

8 C. Ehrhardt and R. Ahlrichs, *Theor. Chim. Acta*., 1985, **68**, 231–245.