Supporting Information

Synthesis, Characterization and Magnetic Properties of Head-to-Head Stacked Vanadocenes

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Broken-Symmetry structure of 3

$E_{\text{tot}} = -3046.31948234331$ a.u.

V	5.87133800	4.54895000	1.56754100
C	8.04164900	5.19458500	1.97157700
C	7.55310900	4.46394200	3.09336500
C	7.25834600	3.14105900	2.67788200
C	7.54263300	3.04278500	1.29148600
C	8.01163200	4.30732300	0.85259700
H	8.33513200	4.55313000	-0.14869500
C	3.83468700	5.16533800	2.37243400
C	4.27841400	6.17532000	1.47928200
H	4.49878900	7.20047400	1.73896600
C	4.39186000	5.59839600	0.18684800
H	4.69945100	6.11059300	-0.71332900
C	4.01860700	4.23150500	0.28158800
C	3.67401600	3.96402000	1.63237000
C	8.43583700	6.61946400	1.92946400
H	7.43702800	4.85503400	4.09287600
H	6.87669900	2.35045400	3.30719500
H	7.42472700	2.16219600	0.67678200
H	3.65410200	5.28861300	3.43033600
H	3.99992000	3.52059800	-0.53169800
H	3.34883000	3.01276200	2.02791900
C	7.95866600	7.37241100	0.86897800
C	9.19044100	7.27682600	2.96388600
H	7.39159900	6.86402500	0.09627400
C	8.09904300	8.76650000	0.80685300
C	9.94506800	6.61942500	3.99832400
C	9.19045300	8.71629200	2.96391000
H	7.70515000	9.30981300	-0.04453800

C	8.65657700	9.43149500	1.86638000
C	10.42224600	7.37241100	5.05885000
C	10.33925800	5.19460800	3.95622600
C	9.72432000	9.43149100	4.06142900
H	8.69867700	10.51526900	1.88626200
H	10.98928700	6.86405200	5.83149800
C	10.28182500	8.76650600	5.12088900
V	12.50956900	4.54892900	4.36026900
C	10.82779700	4.46396200	2.83436900
C	10.36923000	4.30734300	5.07522900
H	9.68220200	10.51528300	4.04152400
H	10.67575200	9.30982500	5.97232700
C	11.12254900	3.14106900	3.24991100
C	10.83827300	3.04274700	4.63631100
H	10.04576100	4.55311300	6.07646600
C	14.54620100	5.16534000	3.55537600
C	14.10248500	6.17532700	4.44851700
H	13.88211900	7.20046100	4.18884800
C	13.98905000	5.59839100	5.74094800
H	13.68146800	6.11059200	6.64113800
C	14.36228800	4.23148700	5.64626100
C	14.70690200	3.96398600	4.29538100
H	10.94389700	4.85503000	1.83493600
H	11.50420800	2.35046900	2.62059600
H	10.95615000	2.16220700	5.25098200
H	14.72678900	5.28861700	2.49745300
H	14.38099600	3.52060600	6.45948300
H	15.03205700	3.01278000	3.89987300

Synthesis of bis(μ_2-chlorido)bis((η^5-cyclopentadienyl)tetrahydrofuranvanadium(II)) (2)[1]

A mixture of potassium (0.67 g, 17 mmol) and naphthalene (2.2 g, 17 mmol) in thf (35 mL) was stirred at −15 °C for 4.5 h. Solid vanadocene (1.4 g, 7.8 mmol) was added to the green solution and the reaction mixture was allowed to stir 17 h at room temperature. The yellow solution was cooled to −78 °C for 8.5 h leading to precipitation of potassiumcyclopentadienide which was removed *via* filtration. 1,2-Dichloroethane (0.31 mL, 3.9 mmol) was added to the filtrate at 0 °C and the mixture was stirred for 30 min. The solvent was removed under reduced pressure and the red residue was extracted with *n*-hexane (40 mL). Addition of thf (1.4 mL, 21 mmol) and 1,2-dichloroethane (0.31 mL, 3.9 mmol) led to crystallization of the desired product at room temperature. The solvent was decanted and the crystals were washed with *n*-pentane (20 mL). The complex **2** was obtained as a violet, crystalline solid (0.95 g, 4.3 mmol, 54 % (69 %)[1]). ^{1}H NMR (400 MHz, toluene-d$_8$, 25 °C) δ = 124.72 (bs), 3.72 (bs, 4H, thf-α), 1.52 (bs, 4H, thf-β). ^{1}H NMR (400 MHz, thf-d$_8$, 25 °C) δ = 125.92 (bs).

Spin densities and MO occupations for different bismetallocene complexes

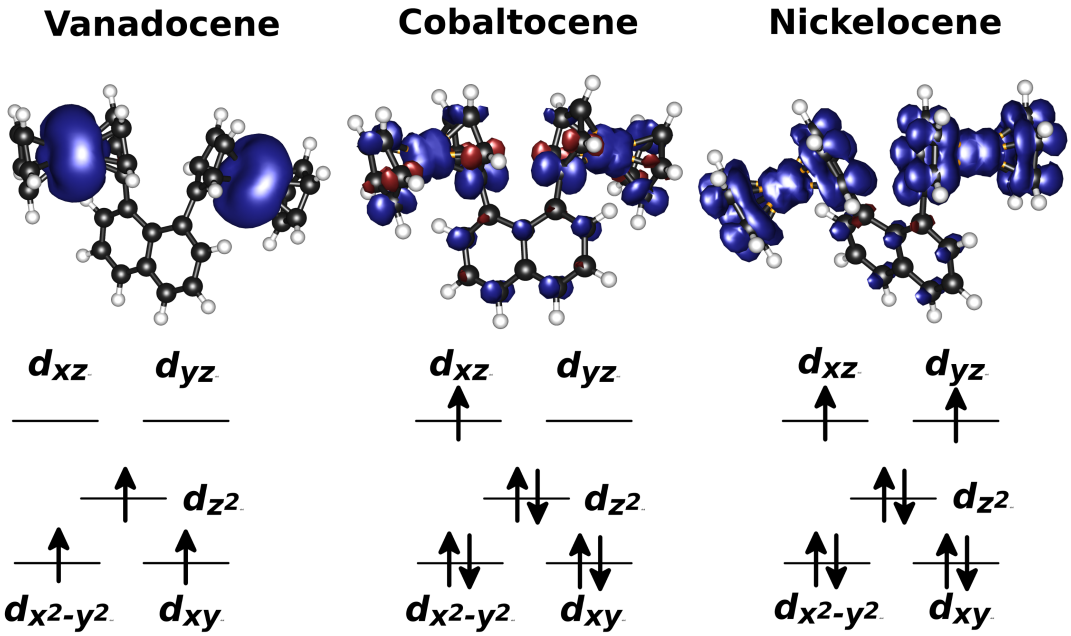

Figure SI1: Spin distributions for bismetallocene complexes differing in the central metal ions (top) calculated with TPSSH/def2-TZVP in the high-spin state and occupation schemes of for the d orbitals in metallocenes (bottom).

Crystal Parameter

Table SI1: Selected interplanar and torsional angles [°] and interatomic distances [Å] of **2**, $[V(\mu_2\text{-Cl})(\eta^5\text{-Cp}(CH_2)_2NMe_2)]_2$[2] and $[V(\mu_2\text{-Cl})(\eta^5\text{-Cp})(PEt_3)]_2$[3]; plane[4]: best-fit plane through corresponding atoms.

	2	$[V(\mu_2\text{-Cl})(\eta^5\text{-Cp}(CH_2)_2NMe_2)]_2$[2]	$[V(\mu_2\text{-Cl})(\eta^5\text{-Cp})(PEt_3)]_2$[3]
V1–V2	3.4123(2)	3.0144(18)	3.2452(22)
V1–Cl1; V1–Cl2; V2–Cl1; V2–Cl2	2.4564(3); 2.4475(3)	2.4430(22); 2.4334(22); 2.4301(23); 2.4537(20)	2.4391(31); 2.4388(29); 2.4375(31); 2.4527(30)
V1–O1/N1/P1; V2–N2/P2	2.1456(8)	2.2506(48); 2.2570(69)	2.5100(41); 2.5094(35)
V1–Cp(C1–C5); V2–Cp(C6–C10)	2.279(13)-2.3036(12)	2.252(69)–2.326(7); 2.2451(76)–2.3117(69)	2.2353(101)–2.2700(98); 2.2438(112)–2.2839(103)
V1–plane_{C1-C5}; V2–plane_{C6-C10}	1.9519(2)	1.9470(12); 1.9324(13)	1.9406(16); 1.9570(16)
Cl1–V1–Cl2; Cl1–V2–Cl2	91.815(10)	92.778(70); 92.596(72)	87.179(93); 86.904(91)
V1–Cl1–V2; V1–Cl2–V2	88.185(10)	76.422(64); 76.164(65)	83.435(92); 83.124(92)
O1/N1/P1–V1–Cl1; O1/N1/P1–V1–Cl2; N2/P2–V2–Cl2; N2/P2–V2–Cl1;	89.78(2); 89.39(2)	93.432(150); 93.798(141); 91.213(171); 100.215(180)	94.046(87); 94.843(90); 96.293(91); 91.508(87)
plane_{C1-C5}–plane_{C6-C10}	0.000(67)	75.428(264)	64.011(431)
$\text{plane}_{Cl1,V1,Cl2}$–$\text{plane}_{Cl1,V2,Cl2}$	0.000(5)	53.049(67)	47.212(80)

Table SI2: Selected interplanar and torsional angles [°] and interatomic distances [Å] for **3** and $[CoCo]_2$[5], $[CoCo]_2^*$[5] and $[NiNi]_2^*$[6] obtained from X-ray structure analysis and from the structure optimization of the BS determinant with TPSSH / def2-TZVP; cent[4]: centroid of the corresponding Cp ligand; plane[4]: best-fit plane through corresponding atoms.

	3	**3**(DFT)	$[CoCo]_2$	$[CoCo]_2^*$	$[NiNi]_2^*$
M1–M1a	7.1212(3)	7.20	6.7392(4)	6.7244(7)	6.9705(3)
C7–C7a	2.9741(13)	3.04	2.9400(19)	3.0176(43)	2.9873(23)
C1–C1a	2.5650(13)	2.56	2.5594(19)	2.5633(45)	2.562(3)
C1–C7	1.4861(13)	1.48	1.4811(19); 1.4801(19)	1.4814(39); 1.4824(37)	1.482(3); 1.478(3)
M1–Cp_{C7-C16}	2.2615(9)–2.2934(10)	2.27–2.30	2.0799(16)–2.1782(14)	2.0654(26)–2.1753(26)	2.1527(15)–2.2548(15)
$plane_{C7-C11}$–$plane_{C7a-C11a}$	26.677(42)	32.69	28.456(57)	33.734(107)	31.480(73)
$plane_{C7-C11}$–$plane_{C1-C6}$	47.927(39)	42.57	40.280(48); 42.516(48)	28.025(96); 28.967(93)	42.397(62); 42.893(63)
$cent_{C7-C11}$–$cent_{C12-C16}$	3.8579(1)	3.86	3.4593(1); 3.4587(1)	3.4425(2); 3.4396(2)	3.637(1); 3.629(1)
C7–C1–C1a–C7a	27.188(76)	27.09	29.655(111)	36.799(229)	27.564(134)
C7–$cent_{C7-C11}$–$cent_{C12-C16}$–C13	20.770(69)	14.91	3.969(97); 17.876(97)	18.551(189); 15.703(186)	10.939(115); 31.447(111)
C2–C3–C3a–C2a	14.404(86)	12.55	15.037(121)	19.307(264)	11.513(144)
M1–H2	3.2119(2)	3.14	3.3117(2); 3.3619(2)	3.5997(4); 3.6191 (4)	3.2245(2)–3.2252(2)

Table SI3: Crystallographic Data and Experimental Parameter for Compounds **2** and **3**

Compound (CCDC)	**2** (1554540)	**3** (1554539)
Empirical formula	$C_{18}H_{26}Cl_2O_2V_2$	$C_{30}H_{24}V_2$
Formula weight	447.17	486.37
Temperature [K]	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a [Å]	8.1826 (1)	18.4035(4)
b [Å]	10.4231 (2)	10.1646(2)
c [Å]	11.7182 (2)	11.8559(3)
α [°]	90	90
β [°]	104.37	90.2150(10)
γ [°]	90	90
Volume [Å^3]	968.15(3)	2217.80(9)
Z	2	4
D_{calc} [g/cm^3]	1.534	1.457
Absorption coefficient μ [mm^{-1}]	1.249	0.859
$F(000)$	460	1000
Crystal size [mm^3]	0.24 × 0.17 × 0.05	0.22 × 0.16 × 0.04
Θ range for data collection [°]	3.23 to 33.50	2.21 to 32.50
Index ranges	−12<=h<=12 −16<=k<=16 −18<=l<=17	−27<=h<=27 −15<=k<=15 −17<=l<=17
Reflections collected	25226	25689
Independent reflections (R_{int})	3731 (0.0232)	3928 (0.0223)
Completeness [%] (to Θ = [°])	98.0 (33.50)	98.0 (32.50)
Max. and min. transmission	0.9402, 0.7537	0.9665, 0.8336
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3731 / 0 / 109	3928 / 0 / 146
Goodness-of-fit on F^2	1.037	1.031
Final R indices [$I > 2sigma(I)$]	$R1$ = 0.0283, $wR2$ = 0.0700	$R1$ = 0.0274, $wR2$ = 0.0697
R indices (all data)	$R1$ = 0.0312, $wR2$ = 0.0720	$R1$ = 0.0315, $wR2$ = 0.0729
Largest diff. peak and hole [eÅ^{-3}]	0.942, −0.309	0.517, −0.238

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