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Chlorodicyclopentadienyloxoniobium(V) complexes revisited: the origin of the asymmetry in the ^{1}H- and ^{13}C-NMR spectra, X-ray crystal structures and ab initio/HF and DFT/B3LYP calculations

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Abstract

^{1}H- and ^{13}C-NMR spectra of chlorodicyclopentadienyloxoniobium(V) complex **I** and its four 1,1′-dialkyl substituted derivatives **II**–**V** have been recorded and assigned based on DQF ^{1}H,^{1}H-COSY and PFG ^{1}H,^{13}C-HMQC and HMBC experiments. Non-equivalences of all cyclopentadienyl protons and carbons in **II**–**V** (as reflected by their different ^{1}H- and ^{13}C-NMR chemical shifts) are explained by synchronous and out-of-phase rotations of the substituted cyclopentadienyl rings. A non-equivalence of the methyls in **III** (1,1′-di-isopropyl) is explained by a detailed inspection of the rotamers of the isopropyl groups. The X-ray structural data show that **III** and **IV** (1-methyl-1′-*tert*-butyl) crystallize in the monoclinic $P2_1/m$ no. 14 (with crystallographic mirror plane) and in the triclinic $P\bar{1}$ no. 2 space groups, respectively. Ab initio/HF and DFT/B3LYP calculations gave energetically optimized structures close to those obtained by X-ray structural analyses. Further, calculated and experimental ^{13}C-NMR chemical shifts are comparable for a majority of carbons.

Keywords: Niobium; Cyclopentadienyl; Oxide; NMR; Crystal structure; Conformations; Ab initio/HF; DFT/B3LYP

1. Introduction

Since their first reported syntheses [1,2] chlorodicyclopentadienyloxoniobium(V) complexes have been a topic of spectroscopic, X-ray crystal structural and theoretical studies [3–8]. In a recent paper Perjéssy et al. correlated the IR and ^{13}C-NMR spectral data of chloro(1,1′-dialkyldicyclopentadienyl)oxoniobium(V) complexes with their theoretical parameters obtained by calculations at the MMX and EHT levels [8]. However, to our knowledge detailed ^{1}H- and ^{13}C-NMR spectral analyses including the explanation for the origin of the asymmetry observed by the ^{1}H- and ^{13}C-NMR spectra [4,8] of these flexible molecules is still lacking. Moreover, theoretical calculations with more modern and sophisticated methods than EHT such as ab initio/Hartree–Fock (HF) and DFT levels along with previously unpublished single-crystal X-ray structural and high field (11.8 T) NMR data available in our laboratories prompted us to make a revisited study of this interesting topic.

2. Results and discussion

The structures of **I**–**V** are described in Scheme 1. The experimental ^{1}H- and ^{13}C-NMR chemical shifts of **I**–**V** are shown in Tables 1 and 2. In addition, calculated ^{13}C-NMR chemical shifts for the energetically optimized structures of **III** and **IV** are included in Table 2. The parent compound **I** gave singlet resonance lines in both ^{1}H- and ^{13}C-NMR experiments. This means that all protons and carbons of the unsubstituted cyclopentadienyl rings of **I** are equivalent. This finding is differ-

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ent from the results described in a previous paper [8] where the carbons of **I** were reported to be non-equivalent in DMSO. In our present study the equivalence of all protons and carbons of **I** was unambiguously detected both in $CDCl_3$ and DMSO-d_6. In the case of substituted congeners **II**–**V** the situation is changed and all cyclopentadienyl protons and carbons are non-equivalent in agreement with the previous reports [4,8]. A previously unreported feature in the ^{1}H- and ^{13}C-NMR spectra of **III** (1,1′-di-isopropyl) is also the non-equivalence of the chemical shifts of the methyls of the isopropyl groups.

If monosubstituted cyclopentadienyl rings in **II**–**IV** are rotating freely and quickly on the NMR time scale they should give by their symmetry properties (C_2) only two chemical shifts in proton and three chemical shifts in carbon resonances. However, the intra-ring C_2-plane of symmetry of the monosubstituted five-membered rings vanishes if the rings are rotating more or less synchronously but in different phases (or out-of-phase) with respect to each other. This behaviour can arise due to steric crowding between the substituted rings which excludes some of their eclipsed conformations. For example, two isopropyls of **III** cannot be eclipsed in a conformation where both of the dihedral angles Cnt′–Nb(1)–Cnt–C(6) and Cnt–Nb(1)–Cnt′ –C(6′) are 0° or close to it at the same time (Cnt = centroid of the cyclopentadienyl ring, (see Fig. 2(a)). In the case of the unsubstituted compound **I** there is no such steric restriction for free rotation of the rings. Therefore in **I** both rings can rotate independently and unsynchronously, thus time-averaging all protons and carbons to become equivalent on the NMR time scale at 30°C as is manifested in the present experiment.

In order to explain the observed non-equivalence of the methyls in **III** a detailed conformational inspection is needed. Fig. 1 describes three rotamers (a–c) of **III** around the rotation of C(isopropyl-C(Cp)-axis). As can

Table 1
^{1}H-NMR data of **I**–**V** measured in $CDCl_3$

Compound				δ(^{1}H) (ppm)				
	R	R′	CH_3	CH	H(2)	H(3)	H(4)	H(5)
I	H	H			6.39	6.39	6.39	6.39
I [a]	H	H			6.45	6.45	6.45	6.45
II	CH_3	CH_3	2.17		5.99	6.09	5.96	6.05
III	$CH(CH_3)_2$	$CH(CH_3)_2$	1.210,1.214	2.92	6.10	6.09	5.98	6.12
IV	CH_3		2.14		5.98	6.04	5.95	6.03
		$C(CH_3)_3$	1.30		6.34 [b]	5.84 [c]	6.10 [c]	6.38 [b]
V	$C(CH_3)_3$	$C(CH_3)_3$	1.29		6.29 [b]	5.94 [c]	5.98 [c]	6.34 [b]

[a] Measured in DMSO-d_6.
[b] Assignments of H-2 and H-5 may be interchanged.
[c] Assignments of H-3 and H-4 may be interchanged.

Table 2
^{13}C-NMR chemical shifts of **I**–**V** measured in $CDCl_3$ and calculated by ab initio/HF and DFT/B3LYP for **III** and **IV**

Compound			δ(^{13}C) (ppm)							
	R	R′	CH_3	C	CH	C(1)	C(2)	C(3)	C(4)	C(5)
I exp.	H	H				114.63	114.63	114.63	114.63	114,63
I [a] exp.	H	H				114.55	114.55	114.55	114.55	114.55
II exp.	CH_3	CH_3	14.52			132.32	106.54	111.97	111.88	117.39
III exp.	$CH(CH_3)_2$	$CH(CH_3)_2$	22.09,22.19		27.98	142.43	103.99	111.21	112.19	114.76
III HF	$CH(CH_3)_2$	$CH(CH_3)_2$	17.96,23.07		20.26	143.76	94.62	111.70	114.90	112.24
III B3LYP	$CH(CH_3)_2$	$CH(CH_3)_2$	19.25,24.39		26.02	138.70	95.30	107.92	114.46	115.63
IV exp	CH_3		14.57			133.32	105.38	112.47	112.88	117.28
		$C(CH_3)_3$	30.26	33.08		144.12	103.04 [b]	108.93 [c]	117.46 [c]	113.80 [b]
IV HF	CH_3		16.29			135.48	97.44	111.14	115.38	113.21
		$C(CH_3)_3$	22.44,24.24,31.59	21.05		145.64	95.34	107.70	123.20	106.26
IV B3LYP	CH_3		15.30			130.78	96.77	107.96	106.69	116.62
		$C(CH_3)_3$	22.91,26.43,34.18	29.64		139.43	95.68	105.25	120.01	103.72
V exp.	$C(CH_3)_3$	$C(CH_3)_3$	29.95	33.06		145.25	101.48 [b]	111.35 [c]	114.82 [c]	114.62 [b]

[a] Measured in DMSO-d_6.
[b] Assignments of H-2 and H-5 may be interchanged.
[c] Assignments of H-2 and H-5 may be interchanged.

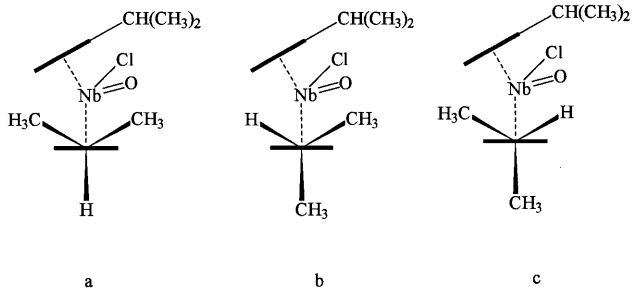

Fig. 1. Three rotamers (a–c) of **III** (around rotation of C(isopropyl)–C(Cp) axis) explaining the non-equivalence of the methyls in the isopropyl group.

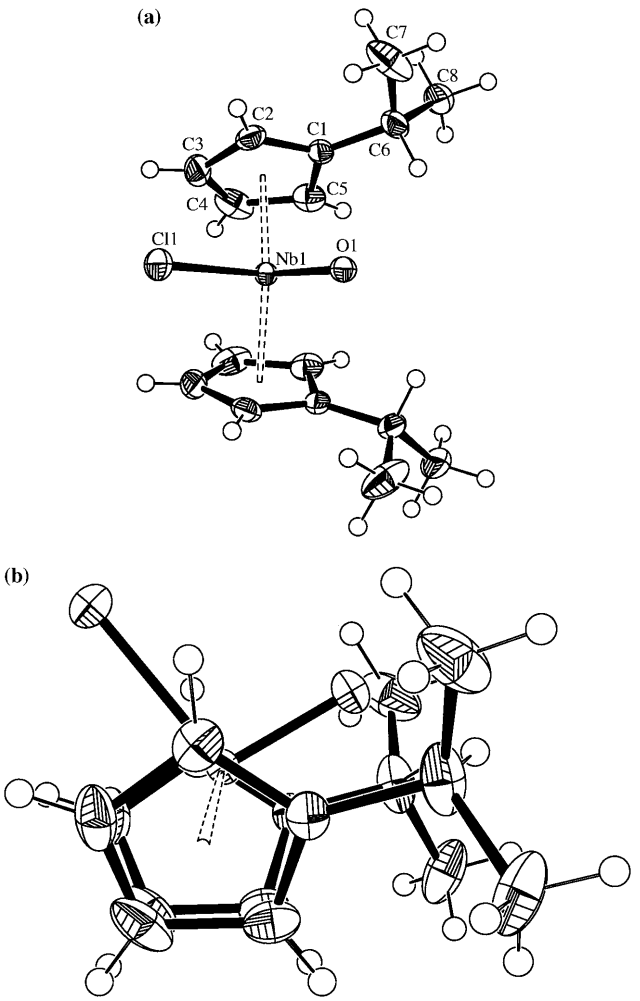

Fig. 2. (a) ORTEP-III plot of **III**. (b) ORTEP-III plot of **III**. A crystallographic mirror plane dictates the eclipsed conformations of cyclopentadienylide rings.

be seen in each rotamer the environment of both methyls is different. Consequently, a fast rotation (in NMR time scale) of the isopropyl group does not time-average these equivalent methyls. However, in the case of $R = CX_3$ ($X = H$ or CH_3) substituted congeners, [**II** ($R = CH_3$, $R' = CH_3$); **IV** ($R = CH_3$, $R' = C(CH_3)_3$) and **V** ($R = C(CH_3)_3$, $R' = C(CH_3)_3$] this non-equivalence inside the alkyl substituents disappears and as the present experiments show only singlet lines from each type of methyl group both in the ^{1}H- and ^{13}C-NMR are observed.

Figs. 2(a,b) and 3 show the ORTEP-III plots [9] and the crystal packing of **III**. Fig. 4(a,b) shows the ORTEP-III plots of **IV**. The crystal data and the structure refinement parameters [10,11] of **III** and **IV** as well as their selected bond lengths and angles are shown in Tables 3 and 4. For comparison the same structural parameters for **I** and **II**, taken from the literature [6,7], are also included. Furthermore, Table 4 shows the corresponding ab initio/HF and DFT/B3LYP optimized structural parameters. As can be seen the majority of bond lengths and angles are comparable in **I**, **II**, **III** and **IV**. Both **III** and **IV** also have typically bent metallocene structures as in **I** and **II** [6,7] with centroid–metal–centroid angles of 129.22 and 129.28°, respectively. When projected down the centroid–centroid vector, an interesting difference between **III** and **IV** is that in **III** the conformations of the cyclopentadienyls are eclipsed (as dictated by a crystallographic mirror plane, Fig. 2(b)) differing from those of **I** [6], **II** [7] and **IV** (Fig. 4(b)) where the rings are staggered. The unit cell packing diagram of **III** is shown in Fig. 3. In this packing the stabilizing interactions are H-bond type attractions between cyclopentadienyl protons and the oxygen and chlorine of an adjacent molecule (the interatomic distances C(4*)···O(1) = 3.50 Å and C(4*)···Cl(1) = 3.75 Å) as well as van der Waals interactions between the isopropyl methyls of the adjacent molecules. This is possible because the methyls of the isopropyl groups are pointing away from the O(1)–Nb(1)–Cl(1)– plane, the torsion angles C(2)–C(1)–C(6)–C(7) and C(5)–C(1)–C(6)–C(8) are −13.4(3) and 46.5(3)°, and the C(7)···C*(7), C(7)···C*(8) and C(8)···C*(8) distances are 7.27, 7.43 and 7.74 Å, respectively. Furthermore, based on a crystallographic mirror plane in **III** (Fig. 2(b)) both C-4 and C-4′ possess the same interatomic distances to O-1* and Cl-1* of the adjacent molecule. The tight and symmetrical packing with the crystallographic mirror plane of **III** differs significantly from that of the parent compound **I** where edge-to-edge and face-to-face intercations of the cyclopentadienyls between adjacent molecules are the most significant interactions in crystal packing [6]. Similarly, in the less sterically congested complex **II** ($R = CH_3$, $R' = CH_3$) the methyl groups are not eclipsed and there is no crystallographic mirror plane as revealed by X-ray structural analysis [7].

Theoretical calculations also reproduce structural parameters comparable with the experimental ones. Only the calculated cyclopentadienyl centroid–niobium distances are ca. 0.06 Å longer than those obtained by X-ray analysis. On the other hand, the deviations between calculated and experimental bond angles are

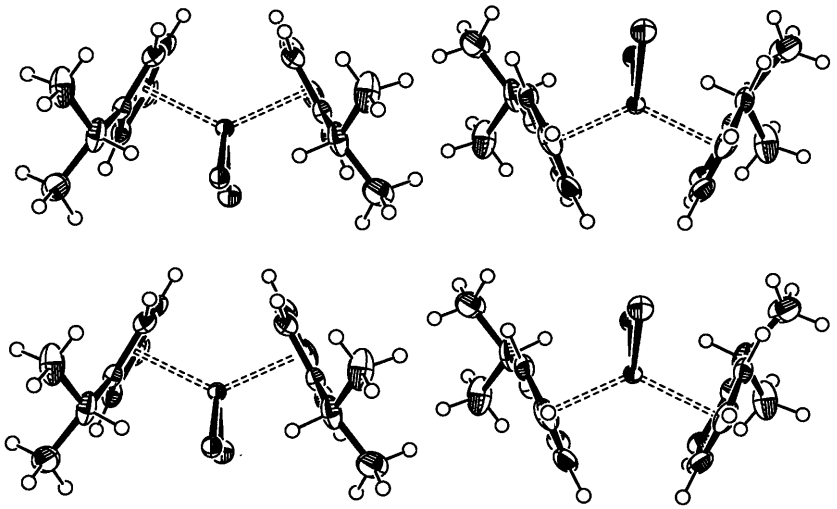

Fig. 3. Unit cell packing diagram of **III**.

insignificant. Also, both ab initio/HF and DFT/B3LYP [12] calculated ^{13}C-NMR chemical shifts (Fig. 2) are in agreement with experimental results, except for C(2) for which theoretical methods systematically gave values which were too small. This discrepancy can be explained by the conformational freedom of the cyclopentadienyl moieties. In calculating ^{13}C-NMR chemical shifts the most energetically stable structure was used. In this conformation C(2) is located close to the oxygen atom which causes increased shielding of C(2) by a through-space mechanism (field effect) as previously explained [8]. The experimental ^{13}C-NMR chemical shift of C(2) (as those of the other carbons) is, however, a statistical average from all conformers of these flexible molecules. Present theoretical calculations at ab initio/HF levels show that a 90° torsion angle of one cyclopentadienyl ring of **III** from its position in the X-ray crystal structure causes only a 12 kJ mol^{-1} increase in the molecular potential energy. Consequently, the difference between the theoretical and experimental ^{13}C-NMR chemical shift of C(2) manifests the conformational freedom of the cyclopentadienyl moieties. For the carbons of the alkyl substituents, DFT/3LYP seems to give more reliable results than the ab initio/HF-method.

3. Experimental

The syntheses and characterization of **I**–**V** were previously reported [2–5].

All ^{1}H- and ^{13}C-NMR spectra were recorded using a Bruker Avance DRX 500 spectrometer equipped with an inverse detection broad-band probehead with a *z*-gradient working at 500.132 MHz in ^{1}H and 125.77 MHz in ^{13}C experiments for 0.1 M $CDCl_3$ solutions at 303 K unless otherwise stated. Detailed lists of all NMR acquisition and processing parameters both for one- and two-dimensional experiments are available on request. Crystal structure data (Table 3) were recorded using a Nonius KappaCCD X-ray diffractometer using

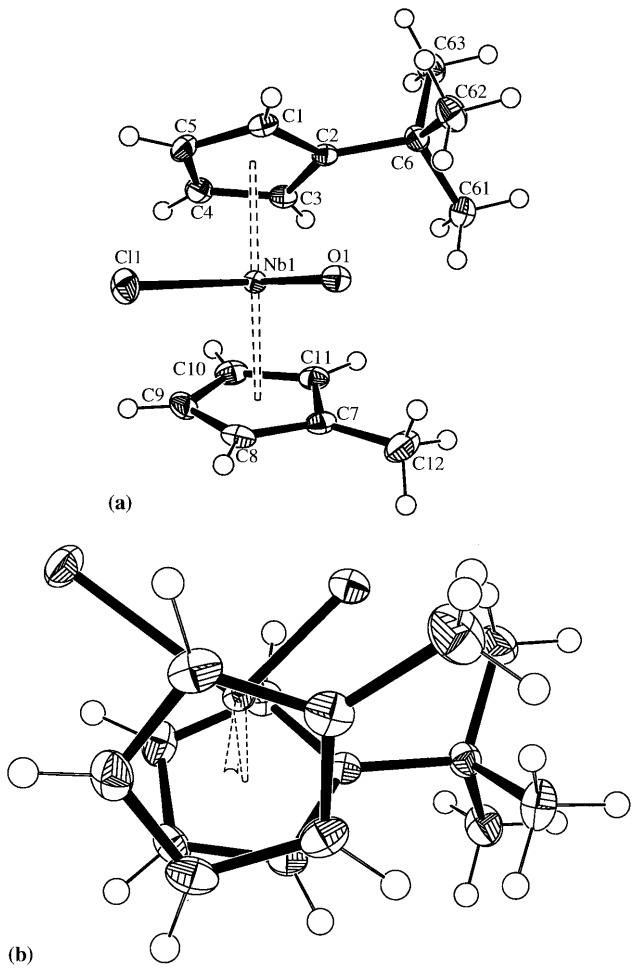

Fig. 4. (a) ORTEP-III plot of **IV**. (b) ORTEP-III plot of **IV** showing staggered conformations of cyclopentadienylide rings.

Table 3
Crystal data and structure refinements [11,12] of **III** and **IV**

	III	**IV**
CCDC deposition number	141156	141155
Empirical formula	$C_{16}H_{22}ClNbO$	$C_{15}H_{20}ClNbO$
Formula weight	358.70	344.67
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/m$ no.14	$P\bar{1}$ no.2
Unit cell dimensions		
a (Å)	6.1553(2)	6.0603(1)
b (Å)	18.838(1)	7.7751(2)
c (Å)	7.1591(3)	16.4460(4)
α (°)	90	78.824(1)
β (°)	111.529(2)	87.275(1)
γ (°)	90	69.737(2)
Volume (Å^3)	772.21(6)	713.02(3)
Z	2	2
D_{calc} (g cm^{-3})	1.543	1.605
Absorption coefficient (mm^{-1})	0.942	1.017
$F(000)$	368	352
Crystal size (mm)	$0.30\times0.20\times0.15$	$0.55\times0.25\times0.05$
Theta range for data collection	3.24 to 27.88°	3.32 to 27.91°
Index ranges	$0\le h\le8$, $0\le k\le24$, $-9\le l\le8$	$0\le h\le7$, $-9\le k\le10$, $-21\le l\le21$
Reflections collected	1883	3307
Completeness to theta	27.88°, 98.8%	27.91°, 96.9%
Max./min. transmission	0.8716, 0.7652	0.9509, 0.6047
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1883/0/135	3307/0/243
Goodness-of-fit on F^2	1.133	1.119
Final R indices [$I>2\sigma(I)$]	$R_1=0.0233$, $wR_2=0.0646$	$R_1=0.0207$, $wR_2=0.0542$
R indices (all data)	$R_1=0.0245$, $wR_2=0.0673$	$R_1=0.0213$, $wR_2=0.0546$
Largest difference peak and hole (e Å^{-3})	0.434 and −0.563	0.358 and −0.529.

graphite monochromatized Mo–K_α radiation ($\lambda=0.71073$ Å) at 173 K.

The ab initio and density functional calculations were performed for complexes **III** and **IV** for comparison with X-ray structures and NMR data using GAUSSIAN-98 software [12] on a Compaq AlphaServer ES40. Ab initio HF and density functional B3LYP methods with the effective core potential LANL2DZ for the Nb atom and standard basis set 6-31G(d) for all other atoms were used for the optimization of the equilibrium geometries, calculation of total energies, ^{1}H- and ^{13}C-NMR chemical shifts. At the beginning the molecular geometry was fully optimized at the HF/3-21G and B3LYP/3-21G levels. Following this the structural optimization was continued at the ab initio HF and density functional B3LYP levels using the basis set 6-31G(d) and the effective core potential LANL2DZ. Finally, the optimized structures were used in computing the ^{1}H- and ^{13}C-NMR chemical shifts

4. Supplementary material

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no.141156 for compound **III** and CCDC no.141155 for compound **IV**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 4
Selected bond lenghts (Å) and angles (°) for **I**, **II**, **III** and **IV**

	I [a]	**II** [b]	**III**			**IV**		
	X-ray	X-ray	X-ray	HF	B3LYP	X-ray	HF	B3LYP
Nb–Cnt [c]	2.171	2.177	2.1702(9)	2.232	2.237	2.1723(8)	2.235	2.234
Nb–Cnt′ [d]	2.182	2.176	2.1702(9)	2.232	2.235	2.1665(8)	2.230	2.241
Nb–O	1.737	1.732	1.7366(17)	1.706	1.748	1.7413(11)	1.706	1.750
Nb–Cl	2.439	2.431	2.4445(7)	2.511	2.464	2.4464(4)	2.512	2.463
O–Nb–Cl	98.4	99.63	98.95(7)	101.5	101.3	98.41(4)	100.5	100.4
O–Nb–Cnt	108.1	107.76	107.68(5)	107.5	106.3	108.33(6)	108.7	109.0
O–Nb–Cnt′	108.2	107.06	107.68(5)	107.5	107.6	106.98(6)	107.3	105.7
Cnt–Nb–Cnt′	128.2	129.15	129.22(6)	130.1	129.9	129.28(7)	129.6	129.5
Cl–Nb–Cnt	104.3	104.09	104.58(5)	103.2	104.4	105.68(6)	103.4	104.2
Cl–Nb–Cnt′	105.5	105.30	104.58(5)	103.2	103.8	103.84(6)	103.3	104.2

[a] Taken from Ref. [6].
[b] Taken from Ref. [7].
[c] Cnt = centroid of the first cyclopentadienylide ring.
[d] Cnt′ = centroid of the second cyclopentadienylide ring.

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