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Fascinating chemistry of mutually compatible symmetrical/ asymmetrical and bulky heterocyclic β-diketones-modified zirconocene dichloride: DFT assisted optimized molecular structure of $C_{33}H_{32}N_2O_4Zr$ containing two unequal Zr-Cp bonds

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Mutually compatible bulky heterocyclic β-diketones and symmetrical/ asymmetrical β-diketones- modified zirconocene dichloride products of the general formula $[Cp_2ZrLL']$ (where LH= $RCO\overline{C:C(OH)N(C_6H_5)N:C}CH_3$ and L'H= $R'COCH_2COR''$, R= $-CH_3$ ($L_{(1)}H$), R= $-CH_2CH_3$ ($L_{(2)}H$), R= $-C_6H_5$ ($L_{(3)}H$), R= *p*-ClC_6H_4- ($L_{(4)}H$) and R'= R''= $-CH_3$ ($L'_{(1)}H$), R'= $-CH_3$, R''= $-C_6H_5$ ($L'_{(2)}H$), R'= R''= $-C_6H_5$ ($L'_{(3)}H$)**)** have been generated by the reactions of zirconocene dichloride with mutually compatible bulky heterocyclic β-diketones and symmetrical/ asymmetrical β-diketones in the presence of triethylamine in 1:1:1:2 molar ratio in refluxing dry THF. On the basis of spectroscopic and mass studies, tentative structures of these complexes have been suggested. Density functional theory (B3LYP) has been employed to study the optimized molecular structure, optimized energy, stability, distortions of optimized geometry and energy gap of one representative zirconocene complex to corroborate the structures of these complexes.

Keywords: Zirconocene complexes, β-Diketones, Unequal Zr-Cp bonds, Optimized energy, Optimized geometry

The fascinating chemistry of zirconocene complexes has been extensively investigated[1-3]. The preparations of zirconocene complexes of various types have been described. A number of organic ligands have been used to modify the reactivity of zirconocene dichloride. β-Diketones[4,5] and heterocyclic β-diketones[6,7] are an important class of chelating ligands and demonstrate keto-enol tautomerism. The presence of electron releasing group and electron withdrawing group has a pronounced effect on tautomeric forms. Among these β-diketones, asymmetrical β-diketones like benzoyl acetone is quite interesting. It is pertinent to examine the direction of enolization towards phenyl group or methyl group in benzoyl acetone[8]. The metal complexes of β-diketones and heterocyclic β-diketones have been reported to exhibit various types of biological activities[9-11]. The complexes derived from zirconocene dichloride demonstrate many applications such as in the preparation of electronic materials[12,13], pharmaceuticals[14-16], agricultural chemicals[17,18], in the field of medicine and technology[19-21]. In the present communication, we report herein mutually compatible symmetrical/ asymmetrical β-diketones and bulky heterocyclic β-diketones – modified zirconocene dichloride products. Recently, DFT has been employed as the widely used scientific technique for the characterization of organic-inorganic hybrid complexes[22,23]. One of the representative zirconocene complex was investigated by DFT (B3LYP) to study the optimized molecular structure, optimized energy, stability, distortions of optimized geometry and energy gap. The presence of various groups such as $-CH_3$, $-CH_2CH_3$, $-C_6H_5$, *p*-ClC_6H_4- and C_5H_5 gave an opportunity to study the steric and electronic effects of these groups on the properties of these zirconocene complexes. DFT assisted optimized molecular structure of a representative zirconocene complex revealed the presence of two unequal Zr-Cp bonds.

Experimental Section

Zirconocene dichloride, symmetrical and asymmetrical β-diketones are commercially available. Bulky heterocyclic β-diketones were prepared by the reported method[24]. Infrared spectra (4000-400 cm^{-1}) of zirconocene complexes were recorded on Shimadzu-Japan 8400s spectrophotometer and the samples were prepared as KBr pellets. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a Jeol-ECS 400 Delta 2_NMR spectrometer. Mass spectra of the complexes were recorded on Waters-G2S-QTOF-YDA 200 mass spectrometer.

A similar method was used to prepare zirconocene complexes. The synthetic details of one representative complex are given and analytical data of other complexes are summarized in Table 1.

Synthesis of $(C_5H_5)_2ZrL_{(4)}L'_{(1)}$, Complex 10

$[ZrCp_2(p\text{-}ClC_6H_4COC{:}C(O)N(C_6H_5)N{:}CCH_3)(CH_3C(O)CHC(O)CH_3)]$

A THF solution of the two organic ligands, bulky heterocyclic β-diketone ($L_{(4)}H$) (0.91g, 2.93mmol) and symmetrical β-diketone ($L'_{(1)}H$) (0.29g, 2.93mmol) was mixed with a THF solution of $(C_5H_5)_2ZrCl_2$ (0.85g, 2.93mmol) followed by drop-wise addition of triethylamine (0.59g, 5.86 mmol). The yellow colour of the solution changed to reddish brown. The reaction contents were refluxed for 8 hours. $Et_3N.HCl$ formed in the reaction was filtered out. The excess THF was removed *in vacuo*. A coloured solid product was obtained. This product was purified by recrystallization from benzene- n-hexane mixture.

Results and Discussion

The reactions of zirconocene dichloride with mutually compatible bulky heterocyclic β-diketones and symmetrical/ asymmetrical β-diketones in the presence of triethylamine in 1:1:1:2 molar ratio in refluxing dry THF afforded the complexes having the general formula $[Cp_2ZrLL']$ **(**where LH=

Table 1 — Analytical data of Zirconocene (IV) complexes of symmetrical/asymmetrical and bulky heterocyclic β-diketones

Complex no.	Complex formula (Empirical formula)	Reagents in g (mmol)				$Et_3N.HCl$ (g) Found (Calcd)	Yield (%)	Zr (%) Found (Calcd)
		Et_3N	LH	L'H	Cp_2ZrCl_2			
1	$Cp_2ZrL_{(1)}L'_{(1)}$ $(C_{27}H_{28}N_2O_4Zr)$	0.62 (6.18)	0.67 (3.09)	0.31 (3.09)	0.90 (3.09)	1.22 (1.23)	62	17.03 (17.04)
2	$Cp_2ZrL_{(1)}L'_{(2)}$ $(C_{32}H_{30}N_2O_4Zr)$	0.69 (6.84)	0.74 (3.42)	0.55 (3.42)	1.00 (3.42)	1.34 (1.36)	64	15.25 (15.27)
3	$Cp_2ZrL_{(1)}L'_{(3)}$ $(C_{37}H_{32}N_2O_4Zr)$	0.58 (5.76)	0.62 (2.88)	0.64 (2.88)	0.84 (2.88)	1.13 (1.14)	69	13.82 (13.83)
4	$Cp_2ZrL_{(2)}L'_{(1)}$ $(C_{28}H_{30}N_2O_4Zr)$	0.65 (6.50)	0.75 (3.25)	0.32 (3.25)	0.95 (3.25)	1.27 (1.29)	67	16.59 (16.60)
5	$Cp_2ZrL_{(2)}L'_{(2)}$ $(C_{33}H_{32}N_2O_4Zr)$	0.76 (7.54)	0.87 (3.77)	0.61 (3.77)	1.10 (3.77)	1.49 (1.50)	62	14.90 (14.92)
6	$Cp_2ZrL_{(2)}L'_{(3)}$ $(C_{38}H_{34}N_2O_4Zr)$	0.58 (5.78)	0.66 (2.89)	0.64 (2.89)	0.84 (2.89)	1.12 (1.14)	59	13.53 (13.54)
7	$Cp_2ZrL_{(3)}L'_{(1)}$ $(C_{32}H_{30}N_2O_4Zr)$	0.66 (6.54)	0.91 (3.27)	0.32 (3.27)	0.95 (3.27)	1.29 (1.30)	61	15.25 (15.27)
8	$Cp_2ZrL_{(3)}L'_{(2)}$ $(C_{37}H_{32}N_2O_4Zr)$	0.61 (6.08)	0.84 (3.04)	0.49 (3.04)	0.89 (3.04)	1.19 (1.21)	64	13.82 (13.83)
9	$Cp_2ZrL_{(3)}L'_{(3)}$ $(C_{42}H_{34}N_2O_4Zr)$	0.76 (7.50)	1.05 (3.75)	0.85 (3.75)	1.11 (3.75)	1.49 (1.50)	65	12.63 (12.64)
10	$Cp_2ZrL_{(4)}L'_{(1)}$ $(C_{32}H_{29}ClN_2O_4Zr)$	0.59 (5.86)	0.91 (2.93)	0.29 (2.93)	0.85 (2.93)	1.14 (1.16)	61	14.42 (14.43)
11.	$Cp_2ZrL_{(4)}L'_{(2)}$ $(C_{37}H_{31}ClN_2O_4Zr)$	0.60 (6.00)	0.94 (3.00)	0.48 (3.00)	0.87 (3.00)	1.17 (1.19)	59	13.13 (13.14)
12	$Cp_2ZrL_{(4)}L'_{(2)}$ $(C_{42}H_{33}ClN_2O_4Zr)$	0.57 (5.64)	0.88 (2.82)	0.63 (2.82)	0.82 (2.82)	1.11 (1.12)	68	12.05 (12.06)

$RCO\overline{C:C(OH)N(C_6H_5)N:C}CH_3$ and L'H= R'COCH$_2$COR", R= $-CH_3$ (L$_{(1)}$H), R= $-CH_2CH_3$ (L$_{(2)}$H), R= $-C_6H_5$ (L$_{(3)}$H), R= p-ClC$_6$H$_4$- (L$_{(4)}$H) and R'= R"= $-CH_3$ (L'$_{(1)}$H), R'= $-CH_3$, R"= $-C_6H_5$ (L'$_{(2)}$H), R'= R"= $-C_6H_5$ (L'$_{(3)}$H)) (Scheme 1).

During these reactions, triethylamine hydrochloride was formed which was filtered out. After removing the excess solvent *in vacuo*, coloured solid products were obtained. These products were purified by recrystallization from benzene-hexane mixture. The tentative structures of these complexes were elucidated by spectroscopic and mass studies.

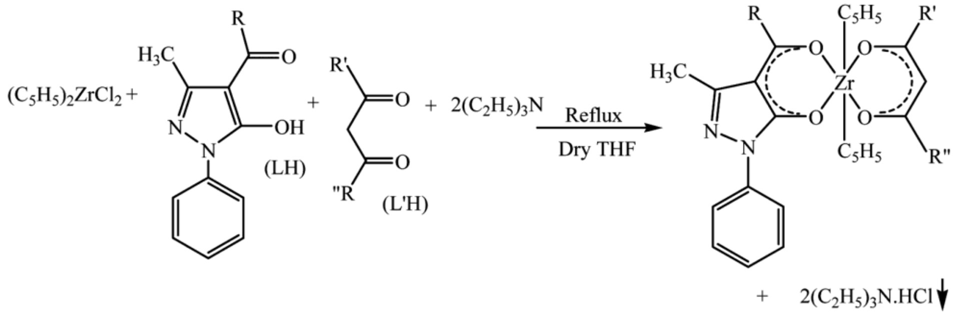
IR spectra

In the IR spectra of mutually compatible bulky heterocyclic β-diketones and symmetrical/ asymmetrical β-diketones- modified zirconocene dichloride products, two new medium intensity bands appeared in the regions 543.93-504.23 cm^{-1} and 639.03-606.11 cm^{-1} which may be assigned to Zr-O bonds. The υ(>C=O) stretching vibration was observed at 1545 cm^{-1} in the IR spectra of bulky heterocyclic β-diketones. The carbonyl frequency was observed in the region 1539.16-1531.26 cm^{-1} in the IR spectra of the complexes. The shift of carbonyl frequency to lower wave number indicates the bidentate nature of these ligands in the complexes. The bands observed at ~1570 cm^{-1} and in the region 1608.99-1599.97 cm^{-1} may be due to υ(>C=C< / >C=N-) and phenyl stretchings, respectively. The IR spectra of symmetrical/ asymmetrical β-diketones exhibit a strong band in the region 1650-1620 cm^{-1} which may be due to υ(>C=O) stretching vibrations. There is some shift in the position of this band in the IR spectra of zirconocene complexes. This band shifts to a lower wavenumber which clearly shows bidentate mode of bonding of these ligands in these complexes.

^{1}H NMR spectra

The ^{1}H NMR spectra of some representative zirconocene complexes are summarized in Table 2.

The broad signals of enolic -OH appeared in the regions δ 11.30-12.18 and δ 15.46-16.16[9] in the ^{1}H NMR spectra of bulky heterocyclic β-diketones and symmetrical/ asymmetrical β-diketones, respectively. These signals were absent in the spectra of zirconocene complexes. This demonstrates the deprotonation of these ligands and the formation of Zr-O bond. The methylene protons of symmetrical/ asymmetrical β-diketones (L'$_{(1)}$H and L'$_{(2)}$H) appeared as a singlet at δ 3.61 and at δ 4.10, respectively. In the spectra of zirconocene complexes, this singlet disappeared. In the spectra of the complexes, methine (=CH-) proton appeared in the region δ5.56-6.28 and aromatic protons were observed as a complex pattern in the region δ7.02-7.99. Aromatic protons of bulky heterocyclic β-diketones and symmetrical/ asymmetrical β-diketones are overlapping in this region. The signals for cyclopentadienyl ring protons were observed in the region δ 6.40-6.56.



where

R= $-CH_3$	R'= R"= $-CH_3$	$(C_5H_5)_2ZrL_{(1)}L'_{(1)}$	Complex 1
R= $-CH_3$	R'= $-CH_3$, R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(1)}L'_{(2)}$	Complex 2
R= $-CH_3$	R'= R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(1)}L'_{(3)}$	Complex 3
R= $-CH_2CH_3$	R'= R"= $-CH_3$	$(C_5H_5)_2ZrL_{(2)}L'_{(1)}$	Complex 4
R= $-CH_2CH_3$	R'= $-CH_3$, R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(2)}L'_{(2)}$	Complex 5
R= $-CH_2CH_3$	R'= R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(2)}L'_{(3)}$	Complex 6
R= $-C_6H_5$	R'= R"= $-CH_3$	$(C_5H_5)_2ZrL_{(3)}L'_{(1)}$	Complex 7
R= $-C_6H_5$	R'= $-CH_3$, R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(3)}L'_{(2)}$	Complex 8
R= $-C_6H_5$	R'= R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(3)}L'_{(3)}$	Complex 9
R= p-ClC$_6$H$_4$-	R'= R"= $-CH_3$	$(C_5H_5)_2ZrL_{(4)}L'_{(1)}$	Complex 10
R= p-ClC$_6$H$_4$-	R'= $-CH_3$, R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(4)}L'_{(2)}$	Complex 11
R= p-ClC$_6$H$_4$-	R'= R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(4)}L'_{(3)}$	Complex 12

Scheme 1 — Synthesis of zirconocene complexes (Complex 1-12)

Table 2 — ^{1}H NMR data of zirconocene complexes and the corresponding ligands in δ (ppm)

Ligand/ Complex (Complex no.)	$RCOC:C(OH)\ N(C_6H_5)N:CCH_3$ (LH)						$R'COCH_2COR''$ (L'H)					C_5H_5
				Terminal groups			OH	CH	CH_2	CH_3	C_6H_5	
	OH	Ring CH_3	Ring C_6H_5	C_6H_5	CH_2	CH_3						
L_1H	11.30 (bs)	2.41 (s)	7.24-7.81 (m)			2.43 (s)						
L_2H	12.18 (bs)	2.42 (s)	7.22-7.81 (m)		2.71, 2.72, 2.74, 2.76(q)	1.19, 1.21, 1.23 (t)						
L_3H	11.82 (bs)	2.12 (s)	7.29-7.87 (m)	*								
$L_1'H^a$							15.46 (bs)	5.52 (s)	3.61 (s)	2.00(s) 2.21(s)		
$L_2'H^a$							16.16 (bs)	6.18 (s)	4.10 (s)	2.22 (s)	7.25-7.95(m)	
$Cp_2ZrL_{(1)}L_{(1)}'$ (1)	-	1.76(s)	7.02-7.99(m)			2.59 (s)	-	5.97 (s)	-	1.89(s), 1.79(s)	*	6.52 (s)
$Cp_2ZrL_{(2)}L_{(1)}'$ (4)	-	1.71(s)	7.13-7.97(m)		2.57 (q) (ur)	1.24, (t) (ur)	-	5.56 (s)	-	2.14(s)		6.55(s) 6.56(s)
$Cp_2ZrL_{(2)}L_{(2)}'$ (5)	-	1.76(s)	7.02-7.98(m)		2.59 (q) (ur)	0.97, 0.95, 0.89(t)	-	6.28 (bs)	-	1.79 (bs)	*	6.45(s)
$Cp_2ZrL_{(3)}L_{(2)}'$ (8)	-	1.87(s)	7.24-7.56(m)	*			-	6.03 (bs)	-	1.92(s)	*	6.40(s), 6.47 (s)

Where * merge with phenyl region, (bs)= broad singlet ,b=broad, s= singlet t = triplet , q=quartet , m=multiplet Ref^a = Ref. 09

LH=$RCOC:C(OH)\ N(C_6H_5)N:CCH_3$ [Where R = $-CH_3$ (L_1H), R = $-CH_2CH_3$ (L_2H), R = C_6H_5(L_3H),

L'H =$R'COCH_2COR''$ [where R' = R" = $-CH_3$ ($L_1'H$), R' = $-CH_3$, R" = $-C_6H_5$ ($L_2'H$)]

^{13}C NMR spectra

The ^{13}C NMR spectrum of one representative zirconocene complex 5, $(C_5H_5)_2ZrL_{(2)}L'_{(2)}$ is summarized in Table 3.

In the ^{13}C NMR spectrum of zirconocene complex, the carbonyl carbon signal shows an upfield shift as compared to its position in the spectra of the parent asymmetrical β-diketone ($L'_{(2)}H$). The carbon signal of >C=O of bulky heterocyclic β-diketone appeared at δ 198.0. There is some shift in the position of this signal in the spectrum of zirconocene complex. These observations suggest the bidentate mode of bonding of these ligands in this complex. The carbon signal of $-CH_2-$ group of asymmetrical β-diketones ($L'_{(2)}H$) was observed at δ 54.70. This signal was absent in the spectrum of zirconocene complex **5**, $(C_5H_5)_2ZrL_{(2)}L'_{(2)}$. The cyclopentadienyl ring carbon signal appeared at δ 119.27 in the ^{13}C NMR spectrum of the complex **5**.

Mass spectra

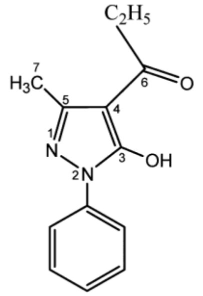
Mass spectra of two representative zirconocene complexes **5** and **11** were recorded.

On the basis of mass and spectroscopic studies, the following plausible structure (Fig. 1) with a distorted octahedral geometry may be suggested for these complexes. The central zirconium is surrounded by two cyclopentadienyl rings and two six-membered rings in the distorted octahedral zirconocene complexes.

DFT Calculations

DFT (B3LYP) method was employed to determine the optimized bond lengths, bond angles, dipole

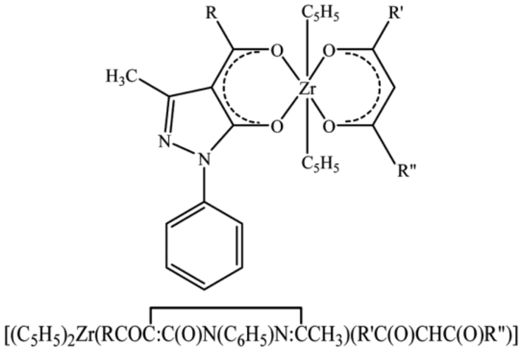
Table 3 — ^{13}C NMR data of the ligands and zirconocene complex in δ (ppm)



L_2H = ; $L_2'H = CH_3COCH_2COC_6H_5$

Ligand/ Complex (Complex no.)	RCOC:C(OH) $N(C_6H_5)N:CCH_3$ (LH)								$R'COCH_2COR''$ (L'H)					
	C_3	C_4	C_5	C_6	C_7	$N\text{-}C_6H_5$	CH_2	CH_3	-CO	-CH-	CH_3	CH_2	C_6H_5	C_5H_5
$L_{(2)}H$[b]	160.4	103.4	137.0	198.0	15.9	147.0,129.0, 126.4,120.8	32.6	8.4						
$L'_{(2)}H$									193.75 183.31	96.64	25.82	54.70	134.85 132.25 128.58 126.97	
$Cp_2ZrL_{(2)}L_{(2)}'$ (5)	159.43	104.54	137.67	198.47	15.7	120.22-148.58	31.6	8.6	191.60 181.67	96.35	26.89	-	*	119.27

* merge with phenyl region
Ref. [b] = Ref. 25



$[(C_5H_5)_2Zr(RCOC{:}C(O)N(C_6H_5)N{:}CCH_3)(R'C(O)CHC(O)R'')]$

where

R= $-CH_3$	R'= R"= $-CH_3$	$(C_5H_5)_2ZrL_{(1)}L'_{(1)}$	Complex 1
R= $-CH_3$	R'= $-CH_3$, R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(1)}L'_{(2)}$	Complex 2
R= $-CH_3$	R'= R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(1)}L'_{(3)}$	Complex 3
R= $-CH_2CH_3$	R'= R"= $-CH_3$	$(C_5H_5)_2ZrL_{(2)}L'_{(1)}$	Complex 4
R= $-CH_2CH_3$	R'= $-CH_3$, R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(2)}L'_{(2)}$	Complex 5
R= $-CH_2CH_3$	R'= R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(2)}L'_{(3)}$	Complex 6
R= $-C_6H_5$	R'= R"= $-CH_3$	$(C_5H_5)_2ZrL_{(3)}L'_{(1)}$	Complex 7
R= $-C_6H_5$	R'= $-CH_3$, R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(3)}L'_{(2)}$	Complex 8
R= $-C_6H_5$	R'= R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(3)}L'_{(3)}$	Complex 9
R= *p*-ClC_6H_4-	R'= R"= $-CH_3$	$(C_5H_5)_2ZrL_{(4)}L'_{(1)}$	Complex 10
R= *p*-ClC_6H_4-	R'= $-CH_3$, R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(4)}L'_{(2)}$	Complex 11
R= *p*-ClC_6H_4-	R'= R"= $-C_6H_5$	$(C_5H_5)_2ZrL_{(4)}L'_{(3)}$	Complex 12

Fig. 1 — Structure of the complex

moments, optimized energy, E_{HOMO}, E_{LUMO} of the ligands, bulky heterocyclic β-diketone ($L_{(2)}H$), asymmetrical β-diketone ($L'_{(2)}H$), zirconocene dichloride and the complex **5**, $(C_5H_5)_2ZrL_{(2)}L'_{(2)}$. The optimized geometry of this complex has also been determined. The optimized data are given in Table 4 and Table 5. The theoretical data obtained from computational calculations are in agreement with the results obtained from experimental studies.

The optimized geometry of one representative zirconocene complex **5**, $(C_5H_5)_2ZrL_{(2)}L'_{(2)}$ was determined with the help of computational work. The optimized structures of $(C_5H_5)_2ZrCl_2$, the ligands, $L_{(2)}H$, $L'_{(2)}H$ and the complex 5, $(C_5H_5)_2ZrL_{(2)}L'_{(2)}$ are shown in Fig. 2, Fig. 3, Fig. 4 and Fig. 5. Tables of DFT data of zirconocene dichloride, organic ligands $L_{(2)}H$, $L'_{(2)}H$ and their corresponding zirconocene complex **5**, $(C_5H_5)_2ZrL_{(2)}L'_{(2)}$ are provided as supplementary material. It is quite interesting to study the chelating behaviour of mutually compatible bulky heterocyclic β-diketone, symmetrical and asymmetrical β-diketones towards zirconocene dichloride and to investigate the optimized geometry of the complex **5**, $(C_5H_5)_2ZrL_{(2)}L'_{(2)}$.

In the complex of the type $(C_5H_5)_2ZrL_{(2)}L'_{(2)}$ (complex **5**), two oxygen atoms of the bulky heterocyclic β-diketone ($L_{(2)}H$), two oxygen atoms

Table 4 — Optimized data of the ligands, heterocyclic β-diketone, asymmetrical β-diketone, Cp_2ZrCl_2 and the complex $Cp_2ZrL_{(2)}L'_{(2)}$

S. No.	Name of ligand / Cp_2ZrCl_2/ Complex	Molecular formula	Energy (au)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE = (E_{LUMO}-E_{HOMO})	Dipole (debye)
$L_{(2)}H$	4-Propanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one	$C_{13}H_{14}N_2O_2$	-763.768985	-6.11	-1.21	4.90	1.74
$L'_{(2)}H$	1-Phenyl-1,3-butanedione	C_6H_7NO	-537.538015	-6.24	-1.79	4.45	3.27
Cp_2ZrCl_2	Bis(cyclopentadienyl)zirconium(IV) dichloride	$C_{10}H_{10}Cl_2Zr$	-1354.25087	-6.67	-2.11	4.56	6.77
$Cp_2ZrL_{(2)}L'_{(2)}$ (Complex 5)	[(4-Propanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-onato)(1-phenyl-1,3-butanedionato)]bis(cyclopentadienyl)zirconium(IV)	$C_{33}H_{32}N_2O_4Zr$	-1733.92597	-4.69	-1.99	2.70	2.3

Table 5 — Optimized bond length and optimized bond angle data of zirconocene complex $Cp_2ZrL_{(2)}L'_{(2)}$ (Complex 5), the corresponding ligands and Cp_2ZrCl_2

$L_{(2)}H$		$L'_{(2)}H$		Cp_2ZrCl_2		$Cp_2ZrL_{(2)}L'_{(2)}$ (Complex 5)	
Atom connectivity	Bond length (Å)	Atom connectivity	Bond length (Å)	Atom Connectivity	Bond length (Å)	Atom connectivity	Bond length(Å)
C11,O2	1.252	C5,O1	1.254	Zr1,Cl1	2.456	Zr1,O1	2.166
C11,C9	1.443	C5,C3	1.439	Zr1,Cl2	2.456	Zr1,O2	2.15
C9,C8	1.407	C3,C7	1.381	Zr1,Lig1	2.265	Zr1,Lig1	3.135
C8,O1	1.323	C7,O2	1.328	Zr1,Lig2	2.265	Zr1,Lig2	2.361
O1,H8	1.011	O2,H23	1.017			Zr1,O3	2.187
						Zr1,O4	2.223
Atom connectivity	Bond angle (°)	Atom connectivity	Bond angle (°)	Atom Connectivity	Bond angle (°)	Atom Connectivity	Bond angle (°)
O2,C11,C9	119.27	O1,C5,C3	122.08	Cl1,Zr1,Cl2	99.18	Lig1,Zr1,O1	88.85
C11,C9,C8	119.43	C5,C3,C7	120.52	Lig1,Zr1,Lig2	129.86	Lig1,Zr1,Lig2	154.88
C9,C8,O1	126.75	C3,C7,O2	120.9			O1,Zr1,O2	78.65
C8,O1,H8	102.69	C7,O2,H23	105.62			O2,Zr1,O4	123.12
						O4,Zr1,O3	78.72
						O3,Zr1,O1	75.11
						Lig2,Zr1,O4	95.15

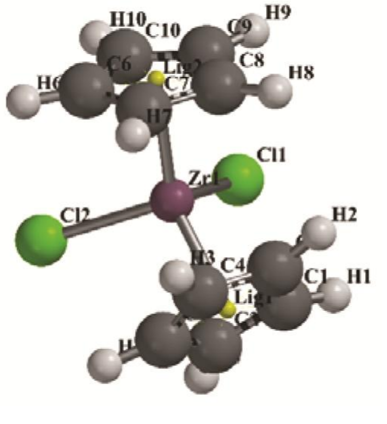


Fig. 2 — Optimized structure of Cp_2ZrCl_2

of asymmetrical β-diketone ($L'_{(2)}H$) and two cyclopentadienyl rings complete the hexacoordination around the central zirconium atom. The six membered bulky heterocyclic β-diketone ($L_{(2)}H$) ring chelates the central zirconium atom by means of two Zr-O bonds. The longer and shorter Zr-O bond lengths are 2.223 Å (Zr1-O4) and 2.187 Å (Zr1-O3), respectively. Another six membered asymmetrical β-diketone ($L'_{(2)}H$) ring chelates the central zirconium atom with two Zr-O bonds. The longer and shorter Zr-O bond lengths are 2.166 Å (Zr1-O1) and 2.15 Å (Zr1-O2), respectively. Of the four Zr-O bond lengths around central zirconium atom, the longest and shortest bond lengths are 2.223 Å (Zr1-O4) and 2.15 Å (Zr1-O2),

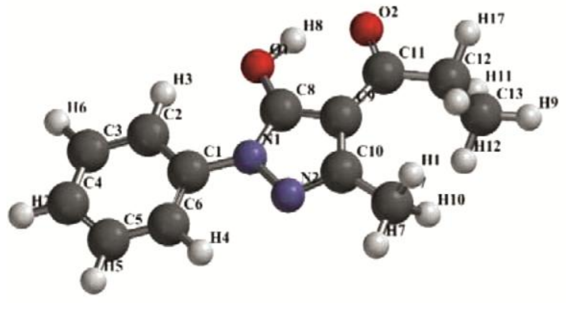


Fig. 3 — Optimized structure of $L_{(2)}H$

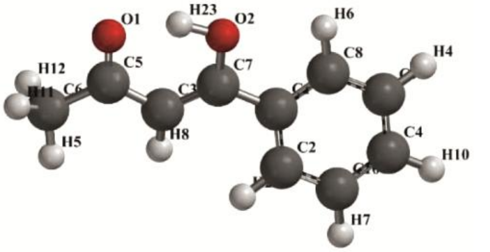


Fig. 4 — Optimized structure of $L'_{(2)}H'$

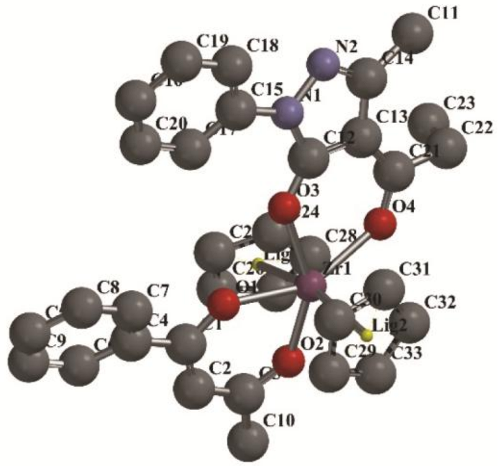


Fig. 5 — Optimized structure of Complex 5, $(C_5H_5)_2ZrL_{(2)}L'_{(2)}$

respectively. The longer and shorter Zr-C_5H_5 bond distances are 3.135 Å (Zr1-Lig1) and 2.361 Å (Zr1-Lig2), respectively. A fascinating and striking feature of this bulky heterocyclic β-diketone and asymmetrical β-diketone- modified product is the presence of unequal Zr1-Lig1 and Zr1-Lig2 bond lengths. It is pertinent to note that Zr1-Lig1 bond length is longer than Zr1-Lig2 bond length. In zirconocene dichloride, both Zr1-Lig1 and Zr1-Lig2 bond distances are the same *i.e*. 2.265 Å, which are elongated in the complex.

The bond angle ∠Lig1-Zr1-Lig2 is 129.86° in $(C_5H_5)_2ZrCl_2$. The bond angle ∠Lig1-Zr1-Lig2 is 154.88° in complex **5**. This indicates that the two cyclopentadienyl rings are distorted.

The chelate bite angle ∠O1-Zr1-O2 of asymmetrical β-diketone ($L'_{(2)}H$) is 78.65° whereas the chelate bite angle ∠O3-Zr1-O4 of bulky heterocyclic β-diketone ($L_{(2)}H$) is 78.72°.

The optimized energies of organic ligands, zirconocene dichloride and the complex may be used as a measure of their stability. The optimized energies of bulky heterocyclic β-diketone ($L_{(2)}H$), asymmetrical β-diketone ($L'_{(2)}H$), zirconocene dichloride and the complex **5**, $(C_5H_5)_2ZrL_{(2)}L'_{(2)}$ are -763.768985 au, -537.538015 au, -1354.25087 au and -1733.92597 au, respectively. These values of the optimized energies clearly demonstrate that the complex **5**, $(C_5H_5)_2ZrL_{(2)}L'_{(2)}$ is the most stable.

Conclusion

The present investigation deals with the generation and spectroscopic characterization of some zirconocene complexes. Mutually compatible bulky heterocyclic β-diketones, symmetric/ asymmetric β-diketones- modified zirconocene dichloride products were obtained by the reactions of zirconocene dichloride with the aforementioned ligands in the presence of triethyl amine in refluxing dry THF. Plausible structures suggested by spectroscopic and mass studies, were corroborated by DFT (B3LYP) investigation of a representative complex **5**, $(C_5H_5)_2ZrL_{(2)}L'_{(2)}$. The optimized molecular structure, optimized energy, optimized geometry and stability of this complex were studied by computational method. A fascinating feature of this complex is the presence of two unequal Zr-Cp bonds.

Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

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