New mixed ligand complexes of dicyclopentadienyl titanium(IV) derived from sterically congested heterocyclic β-diketones and N-protected amino acids

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New mixed ligand monomeric complexes of dicyclopentadienyl titanium(IV) of general formula, $[TiCp_2\{RCOC:\overline{C(O)N(C_6H_5)N:C}CH_3\}\{O_2CCHR'\overline{NC(O)C_6H_4C}(O)\}]$ [where R = $-C_6H_5$, $-CH_3$ and $-C_2H_5$ and R' = –H, $-CH_2C_6H_5$, $-CH_3$ and $-CH(CH_3)_2$] have been synthesised by the reaction of titanocenedichloride with sterically congested heterocyclic β-diketones and N-protected amino acids in the presence of triethylamine in refluxing THF. Plausible structures for these mixed ligand complexes have been suggested

Keywords: titanocenedichloride, heterocyclic β-diketones, N-protected amino acids

The interaction of titanocenedichloride with various monofunctional bidentate ligands in different stoichiometric ratios affords products of variable compositions depending upon the nature of the ligands and experimental conditions.[1-3] An exhaustive survey of the literature reveals that a large number of dicyclopentadienyl titanium(IV) complexes of the types $[Ti(C_5H_5)_2ClL]$, $[TiC_5H_5ClL_2]$ and $[Ti(C_5H_5)_2L_2]$ (where L = monofunctional bidentate ligand) have been synthesised and extensively studied[4-6] due to their interesting chemistry and applications. Metallocene catalysts[7-9] are put to use for the industrial polymerisation of alkenes.[10-13] It is reported that some of the derivatives of titanocenedichloride exhibit an antitumour effect,[14,15] this has provided an impetus for further studies in this field.

N-protected amino acids and heterocyclic β-diketones are the potential organic ligands which have aroused much interest because of their interesting bonding patterns[16,17] and potential biological applications of their metal complexes.[18-20] Much interest has been focused on the chemistry of complexes of these ligands with group IV and XIV metals.[16,17,21-26] However, there is no literature report on the synthesis of mixed ligand complexes of titanocenedichloride derived from these ligands. As an extension of the work described in our previous communications,[22,27] it was considered relevant to prepare mixed ligand complexes of dicyclopentadienyl titanium(IV) of these potential organic ligands. The present work has the objective of seeking more information concerning the nature of bonding and comparative ligating capability of these ligands towards dicyclopentadienyl titanium(IV).

Results and discussion

Dicyclopentadienyl titanium(IV) complexes of general formula $[TiCp_2LA]$ where

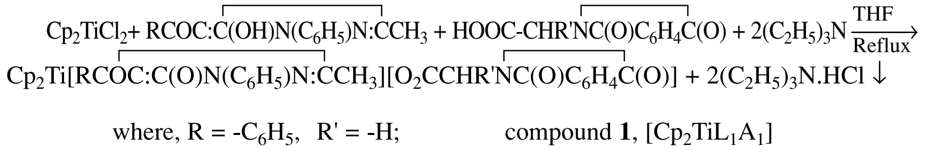
LH= $RCO\overline{C:C(OH)N(C_6H_5)N:C}CH_3$ and

AH = $HOOC-CHR'\overline{NC(O)C_6H_4C}(O)$ [R = $-C_6H_5$, $-CH_3$, $-C_2H_5$ and R' = –H, $-CH_2C_6H_5$, $-CH_3$ and $-CH(CH_3)_2$] have been synthesised by the interaction of titanocenedichloride with congested heterocyclic β-diketones (LH) and N-protected amino acids (AH) in the presence of triethylamine in a 1:1:1:2 molar ratio in refluxing THF solution, see below.

After filtering off triethylamine hydrochloride formed during the reaction and stripping the volatile fraction under reduced pressure, coloured solid powders were obtained which were recrystallised from $CHCl_3$/*n*-hexane mixture in 48 to 56% yield. These solid derivatives have sharp melting points and are highly soluble in common organic solvents like THF, benzene and chloroform. The newly synthesized mixed ligand complexes of dicyclopentadienyl Ti(IV) derived from N-protected amino acids and heterocyclic β-diketones were subjected to spectral (IR, ^{1}H NMR and ^{13}C NMR) studies and information inferred from these studies has been used to diagnose the nature of bonding and to elucidate the plausible structures of these complexes.

IR spectral studies

The IR spectra of these complexes are recorded in the region 4000–400 cm^{-1}. A comparison of IR spectra of these derivatives with the parent ligands furnished useful information regarding



$$Cp_2TiCl_2 + RCOC:\overline{C(OH)N(C_6H_5)N:C}CH_3 + HOOC\text{-}CHR'\overline{NC(O)C_6H_4C}(O) + 2(C_2H_5)_3N \xrightarrow[\text{Reflux}]{\text{THF}}$$
$$Cp_2Ti[RCO\overline{C:C(O)N(C_6H_5)N:C}CH_3][O_2CCHR'\overline{NC(O)C_6H_4C}(O)] + 2(C_2H_5)_3N.HCl\downarrow$$

where, R = $-C_6H_5$,	R' = -H;	compound **1**, $[Cp_2TiL_1A_1]$
R = $-C_6H_5$,	R' = $-CH_2C_6H_5$;	compound **2**, $[Cp_2TiL_1A_2]$
R = $-C_6H_5$,	R' = $-CH_3$;	compound **3**, $[Cp_2TiL_1A_3]$
R = $-CH_3$,	R' = -H;	compound **4**, $[Cp_2TiL_2A_1]$
R = $-CH_3$,	R' = $-CH_2C_6H_5$;	compound **5**, $[Cp_2TiL_2A_2]$
R = $-C_2H_5$,	R' = -H;	compound **6**, $[Cp_2TiL_3A_1]$
R = $-C_2H_5$,	R' = $-CH_2C_6H_5$;	compound **7**, $[Cp_2TiL_3A_2]$
R = $-C_2H_5$,	R' = $-CH_3$;	compound **8**, $[Cp_2TiL_3A_3]$
R = $-C_2H_5$,	R' = $-CH(CH_3)_2$;	compound **9**, $[Cp_2TiL_3A_4]$

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bonding patterns. The appearance of two new medium intensity bands around 620 ± 10 and 540 ± 10 cm^{-1} in these derivatives indicates the formation of Ti-O bonds.[28] In heterocyclic β-diketones, the band at 1545 cm^{-1} is assigned to ν(C=O) stretching and a new band appearing at ~1520 ± 5cm^{-1} due to ν(C$\cdots$O) stretching vibrations in the complexes. This shift in carbonyl frequency (of the order of ~ 20–30 cm^{-1}) to a lower wave number as compared to its position in the free ligands shows that coordination is taking place through carbonyl oxygen of the heterocyclic β-diketones and also reveals the bidentate nature of this ligand. The other bands appearing at ~ 1590 and 1570 cm^{-1} are due to phenyl and ν(C=C/C=N) stretchings and did not show any significant shifting in the complexes.

In the IR spectra of N-protected amino acids, the imido ν(CO)$_{asym}$ and ν(COO)$_{sym}$ vibrations are observed at 1780–1760 cm^{-1} and 1400–1380 cm^{-1}, respectively. The ν(CO)$_{sym}$ and ν(COO)$_{asym}$ merged together in the complexes to give a broad band at 1705–1700 cm^{-1}. In the complexes, the ν(COO)$_{asym}$ band shifts in the region 1730–1710 cm^{-1} indicate the unidentate nature of N-protected amino acids.[16] The magnitude of $\Delta\nu[\Delta\nu=\nu(COO)_{asym}-\nu(COO)_{sym}]$ for these complexes was found to be in the range of 330 to 345 cm^{-1} indicating the unidentate[29] nature of the N-protected amino acids. A medium intensity band due to ν(Ti-ring) vibrations was present at ~ 450 ± 10 cm^{-1} in all these complexes.[30] Other medium intensity bands appearing at ~1060–1020 cm^{-1} and 840–820 cm^{-1} may be assigned to ν(C–H) in plane and ν(C–H) out of plane vibrations, respectively. Another band appearing at ~ 1460–1430 cm^{-1} may be due to ν(C–C) vibration.

NMR spectral studies

The ^{1}H NMR spectra (δ ppm) of complexes and the ligands were recorded in $CDCl_3$ solution using TMS as an internal standard and are summarised in Table 1.

The ^{1}H NMR spectra exhibit the expected signals of the different types of protons present in the complexes. The appearance of a broad singlet (unresolved doublet) in the region δ 6.3–6.7 ppm indicates that the two cyclopentadienyl rings are present in different environments. Other ^{1}H NMR signals of the ligands which do not show significant shifting in the complexes, are summarised in Table 1.

The ^{13}C NMR of some of the representative complexes were recorded in $CHCl_3$ and are summarised in Table 2. A comparison of ^{13}C NMR spectra of the ligands with the corresponding complexes furnished relevant information about the mode of bonding of the ligands with the central titanium atom. Since these mixed ligand complexes are incorporating two potential organic ligands like heterocyclic β-diketones and N-protected amino acids, it is interesting and pertinent to study the coordination behaviour of these ligands towards $Cp_2Ti(IV)$.

In heterocyclic β-diketones ligands of these complexes, the delocalisation of electrons takes place during complex formation which in turn affects the chemical shifts of the carbons. The complex involves a six membered quasiaromatic ring incorporating C_3, C_4, C_6 and the two oxygen atoms. The carbons C_3 and C_4 experience a downfield shift while carbon C_6 shows an upfield shift. These observations reveal the bidentate nature of heterocyclic β-diketone ligand and is consistent with our earlier[17,26] reports. It is also pertinent to study the ligating capability of N-protected amino acids towards $Cp_2Ti(IV)$ in presence of a bulky heterocyclic β-diketone ligand. The ^{13}C NMR spectra of some of these complexes exhibit an upfield shift of ~ 1–3 ppm (Table 2) in the position of the carboxylic carbon signal as compared to its position in the free ligand revealing the unidentate nature of the COO group of the ligand. The unidentate nature of the N-protected amino acid suggests penta coordinated titanium atom in these complexes. In the ^{13}C NMR spectra of complex **1** and complex **4**, the appearance of a doublet for the C_5H_5 protons may be due to the presence of two C_5H_5 rings at axial and equatorial positions in a trigonal bipyramidal geometry. There is no shifting in the position of the imido-carbon appearing around δ 167±1ppm in the N-protected amino acids. This indicates that the imido-carbon is not participating in bonding during complexation. Further, there is no significant shift in other carbon signals of the ligand after complexation (Table 2).

The complexes of the type $[TiCp_2LA]$ where

$LH = RCO\overline{C{:}C(OH)N(C_6H_5)N{:}C}CH_3$ and

$AH = HOOC\ CHR'\overline{NC(O)C_6H_4C}(O)$, were found to be monomeric in nature which rules out the possibility of carboxylate bridging in these complexes. The spectral (IR and ^{13}C NMR) evidences reveal the bidentate nature of heterocyclic β-diketones and unidentate nature of N-protected amino acids. In the ^{1}H NMR spectra of these complexes, the appearance of a broad singlet (unresolved doublet) for Cp protons indicates that the two cyclopentadienyl rings are not present in the same environment. This is further corroborated by the appearance of a doublet for the Cp ring in the ^{13}C NMR specta of complex **1** and complex **4**. On the basis of spectral evidences, the following plausible structure shown in Fig. 1 may be proposed for the complexes of the type $[TiCp_2LA]$ in which the central titanium atom is pentacoordinated and the two Cp rings are occupying axial as well as equatorial positions in the trigonal bipyraminal geometry.

In Fig. 1, each titanium is bonded by one heterocyclic β-diketone ligand and one N-protected amino acid ligand. Each heterocyclic β-diketone is chelated to the central titanium atom with two Ti–O bonds and carboxylic group of the N-protected amino acid is behaving as unidentate ligand.

Experimental

All reactions were carried out in anhydrous conditions. The chemicals used were of reagent grade. $[TiCp_2Cl_2]$ was commercially available. Solvents used were dried by standard methods.[31] The ligands, heterocyclic β-diketones[32] and N-protected amino acids[33-34] used were prepared by reported methods. Triethylamine was distilled over KOH pellets. Melting points were determined in sealed capillaries. Titanium

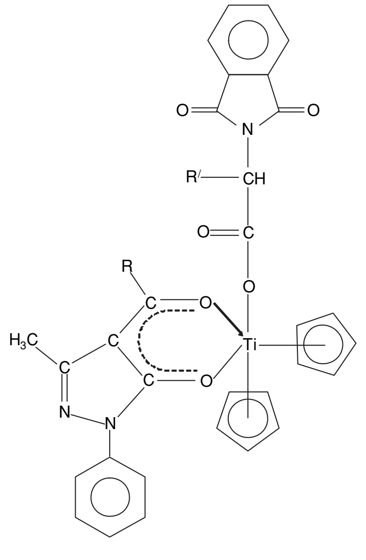


Fig. 1

Table 1 ^{1}H NMR spectral data of heterocyclic β-diketones and N-protected amino acids and their dicyclopentadienyl titanium(IV) complexes (in δ ppm)

Compd no.	Ligands and complexes	RCOC:C(OH)NC$_6$H$_5$N:CCH$_3$(LH)					COC$_6$H$_4$CONCHR′COOH(AH)					C$_5$H$_5$
		OH	Ring Methyl	Phenyl	CH$_2$	Terminal CH$_3$	OH	C$_6$H$_4$/C$_6$H$_5$	CH$_2$	CH	CH$_3$	
	^{a}L$_1$H	12.05(b)	2.10s	7.10–8.04m	–	–						
	^{b}A$_1$H						**	8.05–7.60m	4.47s	–	–	
1	Cp$_2$TiL$_1$A$_1$	–	1.8s (3H)	7.0–8.2m (14H)	–	–	–	*	4.4s (2H)	–	–	6.5s (b) (10H)
	^{c}A$_2$H						9.10s	7.61 m/ 7.11s	3.50d	5.15t	–	
2	Cp$_2$TiL$_1$A$_2$	–	1.8s (3H)	6.7–8.2m (19H)	–	–	–	*	3.5d (2H)	5.13t (1H)	–	6.5s (b) (10H)
	^{a}L$_2$H	10.85(b)	2.51s	6.99–8.04m	–	2.41s						
4	Cp$_2$TiL$_2$A$_1$	–	2.28s	6.7–8.0m	–	2.37s	–	*	4.3s	–	–	6.4s (b)
5	Cp$_2$TiL$_2$A$_2$	–	2.3s(3H)	7.6–8.7m(14H)	–	2.4s(3H)	–	*	3.7d(2H)	5.1t(1H)	–	6.3s (b)(10H)
	^{a}L$_3$H	11.57(b)	2.65s	7.39–8.12m	2.63, 2.71, 2.79, 2.87 q	1.15, 1.23, t 1.31						
6	Cp$_2$TiL$_3$A$_1$	–	2.3s	6.8–8.6m	3.4q	1.3t	–	*	4.2s	–	–	6.5s (b)
7	Cp$_2$TiL$_3$A$_2$	–	2.5s(3H)	7.4–8.3m(14H)	2.8q(2H)	1.1t(3H)	–	*	3.6d(2H)	5.0t(1H)	–	6.7s (b)(10H)
	^{c}A$_3$H						9.27 s	7.87m	–	5.08q	1.74d	
8	Cp$_2$TiL$_3$A$_3$	–	2.5s	7.5–8.3m	2.8q	1.14t	–	*	–	4.9q	1.7d	6.6s (b)
	^{c}A$_4$H						8.94 s	7.80m	–	4.60d 2.70m	1.15d 0.95d	
9	Cp$_2$TiL$_3$A$_4$	–	2.3s	6.8–8.0m	2.7q	1.2t	–	*	–	4.5d 3.7m	1.07d 0.85d	6.3s (b)

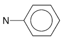
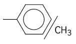
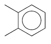
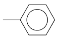
s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, (b) = broad.

*C$_6$H$_4$/C$_6$H$_5$ merged with phenyl region of heterocyclic β-diketones, ** N^{+}H signal appears at 4.2 ppm.

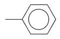
[a]Ref. 17, [b] Ref. 27, [c] Ref. 22,

R = –C$_6$H$_5$(L$_1$H), –CH$_3$ (L$_2$H), –C$_2$H$_5$(L$_3$H) : R′= –H(A$_1$H), –CH$_2$ C$_6$H$_5$(A$_2$H), –CH$_3$ (A$_3$H), –CH(CH$_3$)$_2$ (A$_4$H).

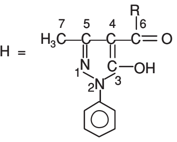
Table 2 ^{13}C NMR data of heterocyclic β-diketones and N-protected amino acids and their dicyclopentadienyl titanium(IV) complexes (in δ ppm)

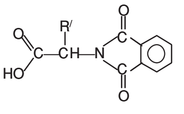
Compd. no.		RCOC:C(OH)NC$_6$H$_5$N:CCH$_3$(LH)							COC$_6$H$_4$CONCHR′COOH(AH)							
	Ligands and Complexes	C$_3$	C$_4$	C$_5$	C$_6$	C$_7$			COO	CO		CH	CH$_2$	CH$_3$		C$_5$H$_5$
	^{a}L$_1$H	161.5	103.6	137.5	191.5	15.7	120.6, 126.5 128.9, 147.9	*								
	^{b}A$_1$H								170.46	169.29	125.25, 134.29 136.03	–	40.25	–	–	
1	Cp$_2$TiL$_1$A$_1$	162.4	107.1	137.30	189.29	15.87	123.43,125.64, 128.10,148.84	*	169.29	167.42	122.99 131.88 133.62	–	38.69	–	–	119.43 121.07
	^{b}A$_2$H								174.06	167.35	123.41 131.26 134.08	52.98	34.24	–	126.7 128.5 128.7 136.5	
2	Cp$_2$TiL$_1$A$_2$	162.82	106.43	137.65	189.34	15.98	123.27, 126.53 128.39, 148.76	*	171.20	167.67	126.38 131.62 133.94	53.18	34.43	–	*	119.91 (b)
	^{c}A$_3$H								174.87	167.28	123.41 131.59 133.94	47.13	–	14.85	–	
3	Cp$_2$TiL$_1$A$_3$	162.22	107.94	137.51	187.77	15.87	122.96, 125.45 128.19, 148.64	*	172.02	167.37	123.41 131.80 133.98	47.25	–	15.06	*	119.10 (b)
	^{a}L$_2$H	160.4	104.1	137.1	196.2	15.4	120.4, 126.1 129.2, 147.0	26.2								
4	Cp$_2$TiL$_2$A$_1$	162.91	105.61	137.08	191.21	15.97	122.17, 126.21 128.53, 147.97	25.43	168.23	167.91	124.25 133.42 134.21	–	38.13	–	–	119.31 120.36

(b) = broad

*Phenyl carbons merged with N 

[a]Ref. 17; [b] Ref. 27; [c] Ref. 22

LH = 

, AH = 

R = -C$_6$H$_5$ (L$_1$H), -CH$_3$ (L$_2$H)

R$^{/}$ = -H(A$_1$H), -CH$_2$C$_6$H$_5$ (A$_2$H),-CH$_3$(A$_3$H)

Table 3 Analytical and physical data of complexes of dicyclopentadienyl titanium(IV)

Compd: no.	Product	Reagents in mmol				% yield (m.p/°C)	Mol. wt. found (Calcd.)	Analysis % found (calcd.)			
		Cp_2TiCl_2	LH	AH	Triethyl-amine			C	H	N	Ti
1	$Cp_2TiL_1A_1$ $C_{37}H_{29}N_3O_6Ti$	6.09	6.09	6.09	12.18	51 (155-158)	646 (659.5)	67.21 (67.38)	4.44 (4.43)	6.29 (6.37)	7.24 (7.26)
2	$Cp_2TiL_1A_2$ $C_{44}H_{35}N_3O_6Ti$	4.03	4.03	4.03	8.06	52 (133-134)	759 (749.7)	70.31 (70.49)	4.72 (4.70)	5.29 (5.60)	6.35 (6.38)
3	$Cp_2TiL_1A_3$ $C_{38}H_{31}N_3O_6Ti$	4.80	4.80	4.80	9.60	55 (158)	677 (673.5)	–	–	-	7.10 (7.10)
4	$Cp_2TiL_2A_1$ $C_{32}H_{27}N_3O_6Ti$	5.00	5.00	5.00	10.00	48 (108-110)	602 (597.4)	64.03 (64.33)	4.49 (4.55)	7.01 (7.03)	8.00 (8.01)
5	$Cp_2TiL_2A_2$ $C_{39}H_{33}N_3O_6Ti$	4.89	4.89	4.89	9.78	49 (170-172)	708 (687.6)	–	–	–	6.95 (6.96)
6	$Cp_2TiL_3A_1$ $C_{33}H_{29}N_3O_6Ti$	4.27	4.27	4.27	8.54	49 (160)	641 (611.5)	64.70 (64.81)	4.80 (4.78)	6.62 (6.87)	7.83 (7.83)
7	$Cp_2TiL_3A_2$ $C_{40}H_{35}N_3O_6Ti$	5.49	5.49	5.49	10.98	53 (162-163)	704 (701.6)	–	–	–	6.81 (6.82)
8	$Cp_2TiL_3A_3$ $C_{34}H_{31}N_3O_6Ti$	6.43	6.43	6.43	12.86	49 (156)	624 (625.5)	–	–	–	7.61 (7.65)
9	$Cp_2TiL_3A_4$ $C_{36}H_{35}N_3O_6Ti$	4.10	4.10	4.10	8.20	56 (112)	668 (653.6)	–	–	–	7.31 (7.32)

$L_1H = C_{17}H_{14}N_2O_2 = C_6H_5CO\mathbf{C}{:}C(OH)NC_6H_5N{:}\mathbf{C}CH_3$

$L_2H = C_{12}H_{12}N_2O_2 = CH_3COC{:}C(OH)NC_6H_5N{:}CCH_3$

$L_3H = C_{13}H_{14}N_2O_2 = C_2H_5COC{:}C(OH)NC_6H_5N{:}CCH_3$

$A_1H = C_{10}H_7NO_4 = \mathbf{C}OC_6H_4CO\mathbf{N}CH_2COOH$

$A_2H = C_{17}H_{13}NO_4 = COC_6H_4CONCH(CH_2C_6H_5)COOH$

$A_3H = C_{11}H_9NO_4 = COC_6H_4CONCH(CH_3)COOH$

$A_4H = C_{13}H_{13}NO_4 = COC_6H_4CONCH(CH(CH_3)_2)COOH$

was estimated gravimetrically as titanium(IV) oxide.[35] IR absorption spectra (4000–400 cm^{-1}) were recorded on a Perkin Elmer Spectrophotometer using nujol mulls. ^1H NMR spectra were recorded in $CDCl_3$ using TMS as an internal reference on JEOL FX 90Q multinuclear spectrometer. ^{13}C NMR were recorded in chloroform solution using tetramethylsilane as an internal reference. Molecular weight measurements were carried out in benzene by determining depression of freezing point. All the derivatives have been prepared by the same procedure. The preparative method of a representative compound is described below and the results for the rest are summarised in Table 3.

Synthesis of $[TiCp_2\ \{C_6H_5COC{:}C(O)N(C_6H_5)N{:}CCH_3\}\ \{O_2CCH_2NC(O)C_6H_4C(O)\}]$: A weighed amount of 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (1.695g, 6.09 mmol) was mixed with the $[TiCp_2Cl_2]$ (1.517g, 6.09 mmol) solution in THF followed by the addition of 1,3-dihydro-1,3-dioxo-2H-isoindole-2-acetic acid (1.249g, 6.09 mmol). After shaking the above reaction mixture, triethylamine (1.232g, 12.18 mmol) was added dropwise. The yellow colour of the reaction mixture changed to dark brown. No heat change was observed during mixing of all the reactants. After refluxing this solution for ~ 7 h., triethylamine hydrochloride was separated which was filtered off. On stripping off the volatile fraction under reduced pressure, a coloured solid was obtained in quantitative yield. The product was recrystallised from $CHCl_3$/*n*-hexane mixture (Yield, 55%). Analytical details and physical properties are listed in Table 3.

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