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SOME BRIDGED $\eta^1:\eta^5$-DICYCLOPENTADIENYLTITANIUM PYRAZOLONE COMPLEXES: SYNTHESES AND STRUCTURAL ELUCIDATION

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Summary

Complexes of the types $(C_5H_5)_2TiClL$, $(C_5H_5)TiClL_2$ and $[(C_5H_4)TiL_2]_2$ (L is a monofunctional bidentate ligand) have been made by reactions of titanocene dichloride with the substituted pyrazolones, $\overline{RCOC{:}C(OH)N(C_6H_5)N{:}C}CH_3$ (where R = CH_3, C_2H_5, C_6H_5 and p-ClC_6H_4) in the presence of triethylamine in refluxing THF. A possible mechanism for the formation of $[(C_5H_4)TiL_2]_2$ is suggested.

Introduction

The preparations of chelated cyclopentadienyltitanium(IV) compounds of the types $(C_5H_5)_2TiClL$, $C_5H_5TiClL_2$ and $(C_5H_5)_2TiL_2$, where L is a monofunctional bidentate ligand, have been described [1–6]. In the reactions of titanocene dichloride with such ligands in 1/2 molar ratio, either one chlorine and one cyclopentadienyl group or both chlorine atoms are ejected, to give $C_5H_5TiClL_2$ or $(C_5H_5)_2TiL_2$ depending upon the identity of the ligand.

We describe below some reactions of titanocene dichloride with substituted pyrazolones.

Results and discussion

The reactions of 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-ones (AcMPPOH) where Acyl = acetyl (AMPPOH), propionyl (PMPPOH), benzoyl (BMPPOH) and p-Cl-benzoyl (CMPPOH) were carried out with titanocene dichloride in 1/1 and 2/1 molar ratios in the presence of Et_3N in anhydrous THF:

$$(C_5H_5)_2TiCl_2 + AcMPPOH + Et_3N \xrightarrow[\text{refluxed}]{\text{THF}} (C_5H_5)_2TiCl(OPPMAc) + Et_3N \cdot HCl\downarrow$$

$$(C_5H_5)_2TiCl_2 + 2BMPPOH + Et_3N \xrightarrow[\text{refluxed}]{\text{THF}} (C_5H_5)TiCl(OPPMB)_2 + Et_3N \cdot HCl\downarrow + C_5H_6\uparrow$$

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The complex $C_5H_5TiCl(OPPMB)_2$ was also synthesized by treatment of $C_5H_5TiCl_3$ with BMPPOH in 1/2 molar ratio in the presence of 2 mol of Et_3N.

$$(C_5H_5)TiCl_3 + 2BMPPOH + 2Et_3N \xrightarrow[\text{refluxed}]{\text{THF}} (C_5H_5)TiCl(OPPMB)_2 + 2Et_3N \cdot HCl\downarrow$$

However, reactions of titanocene dichloride with ligands in 1/2 molar ratio in presence of 2 mol of Et_3N, gave products of the type $[(C_5H_4)Ti(OPPMac)_2]_2$:

$$(C_5H_5)_2TiCl_2 + 2AcMPPOH + 2Et_3N \xrightarrow[\text{refluxed}]{\text{THF}} (C_5H_4)Ti(OPPMAc)_2 + 2Et_3N \cdot HCl\downarrow + C_5H_6\uparrow$$

The compounds $(C_5H_4)Ti(OPPMAc)_2$ were also made by treatment of $(C_5H_5)_2TiCl(OPPMAc)$ with a further mol of ligand in the presence of Et_3N or by treatment of $C_5H_5TiCl(OPPMAc)_2$ with a further mol of triethylamine.

$$(C_5H_5)_2TiCl(OPPMAc) + HOPPMAc + Et_3N \xrightarrow[\text{refluxed}]{\text{THF}} (C_5H_4)Ti(OPPMAc)_2 + Et_3N \cdot HCl\downarrow + C_5H_6\uparrow$$

$$(C_5H_5)TiCl(OPPMAc)_2 + Et_3N \xrightarrow[\text{refluxed}]{\text{THF}} (C_5H_4)Ti(OPPMAc)_2 + Et_3N \cdot HCl\downarrow$$

In these reactions, one of the cyclopentadienyl groups is ejected as cyclopentadiene along with two chlorine atoms. The source of hydrogen for the formation of C_5H_6 is probably the adjacent C_5H_5 ring [7].

The new compounds are solids with colours varying from brown through blackish red to black, and melt with decomposition. They are soluble in common organic solvents and were purified by repeated crystallizations from benzene petroleum ether mixtures. Molecular weight measurements in freezing and in refluxing benzene indicate, that $(C_5H_5)_2TiCl(OPPMAc)$ and $(C_5H_5)TiCl(OPPMB)_2$ are monomeric, but that the complex of composition $(C_5H_4)Ti(OPPMAc)_2$ is dimeric, i.e. is present as $[(C_5H_4)Ti(OPPMAc)_2]_2$.

Spectroscopic data

Infrared data

IR spectra of these compounds show two medium intensity bands in the region 610 ± 10 and 550 cm^{-1} which may be assigned to ν(Ti–O) stretching [8–10]. A band at 1545 cm^{-1} in the spectra of the ligands is due to ν(C=O) [11] stretching. This band is absent from the spectra of the complexes, and a new band which appears at ~ 1515–1525 cm^{-1} may be assigned to ν(C$\overset{...}{=}$O) stretching vibrations [11]. This shift of 20–30 cm^{-1} in the carbonyl frequency indicates that coordination is through carbonyl oxygen of the ligand.

The absence of absorption bands in the region 1675–1655 cm^{-1} rules out the possibility that the ligands are monodentate in these complexes [12]. The bidentate nature of the ligands has also been noted previously [13–15]. The other less significant bands at ~ 1590 and 1575 cm^{-1} are assigned to phenyl and ν(C=C/C=N) stretchings [11] and remain unaltered in the complexes.

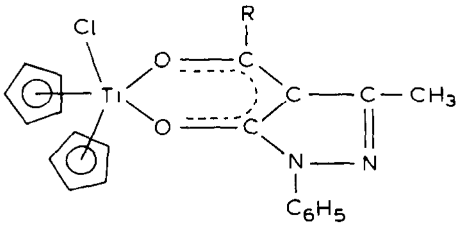
The medium intensity bands observed at ~ 810 and at ~ 1020 cm^{-1} may be assigned to (C–H deformation out of plane) and (C–H deformation in plane) vibrations [16], respectively. The medium intensity band observed at 390 ± 10 cm^{-1} in $(C_5H_5)_2$TiCl(OPPMAc) and (C_5H_5)TiCl$(OPPMB)_2$ derivatives may be assigned to ν(Ti–Cl) stretching [17], this band is absent in the case of the $[(C_5H_4)$Ti(OP-PMAc)$_2]_2$ complexes.

Another medium intensity band, assignable to ν(Ti–ring) vibrations [17], was observed at $\sim 350 \pm 10$ cm^{-1} in all the derivatives. However, for $[(C_5H_4)$Ti-(OPPMAc)$_2]_2$ complexes, a very strong absorption band at $\sim$ 460–465 cm^{-1} due to Ti–C(σ) vibrations [18] was observed in addition to ν(Ti–ring) vibrational band.

Proton Magnetic Resonance spectra

The PMR spectra of the mono-derivatives, $(C_5H_5)_2$TiCl(OPPMAc), (I) show a singlet at δ 1.7 ppm arising from the methyl protons. The multiplets centred at δ 6.5 and at 6.9–8.2 ppm may be assigned to C_5H_5 and phenyl protons, respectively. The appearance of a multiplet instead of a singlet for C_5H_5 protons is due to the presence of two C_5H_5 rings at axial and equatorial positions in a trigonal bipyramidal geometry and to the restricted rotation [19].

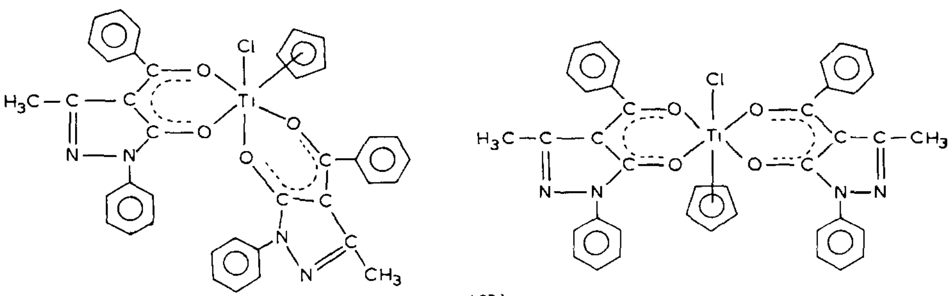
On the basis of the spectral data, the following structure I can be suggested for the $(C_5H_5)_2$TiCl(OPPMAc) derivatives.



(I)

(R = CH_3 , C_2H_5, C_6H_5 and *p*-ClC_6H_4)

The ^{1}H NMR spectrum of the complex, (C_5H_5)TiCl$(OPPMB)_2$, shows a doublet at δ 1.9 ppm due to CH_3 protons of the pyrazolone ring. This splitting of methyl protons indicates that they are in different environments. A singlet at δ 6.5 and a multiplet centred at 6.9–8.2 ppm may be attributed to C_5H_5 and phenyl protons, respectively. This complex could exist in two *trans*- and several *cis*-configurations, and only one of the former would have equivalent methyl groups. However, only one *cis* and one *trans* form are shown here (II).

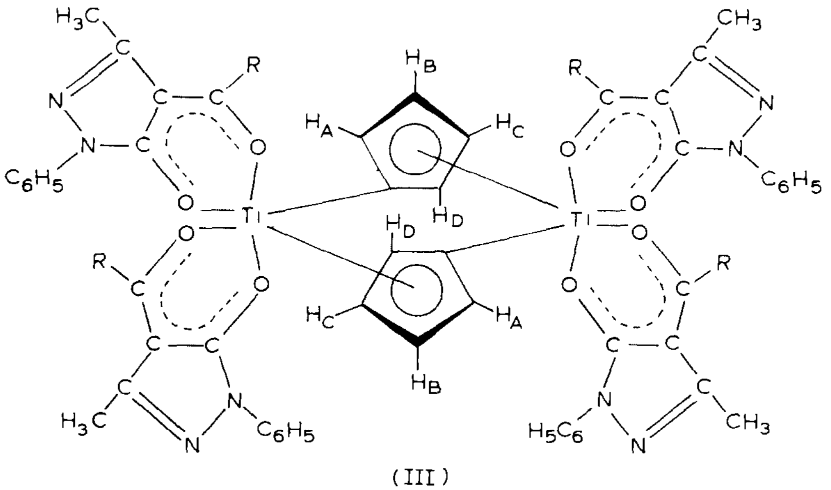


(II)

(*cis*) (*trans*)

Although steric factors will favour the *trans*-geometry, electronic factors should stabilize the *cis*-configuration, which is preferred for this octahedral complex. However, the spectral data does not provide conclusive evidence for the existence of either of the two configurations.

For the derivatives, $[(C_5H_4)Ti(OPPMAc)_2]_2$ a bridged structure, III, in which two $\eta^1:\eta^5$-cyclopentadienyl rings bridge between two titanium atoms are proposed:



(III)

(R = CH_3, C_2H_5, C_6H_5 and *p*-ClC_6H_4)

representative compounds, $[(C_5H_4)Ti(p\text{-}ClC_6H_4COC{:}CON(C_6H_5)N{:}CCH_3)_2]_2$ and $[(C_5H_4)Ti(C_6H_5COC{:}CON(C_6H_5)N{:}CCH_3)_2]_2$. The spectrum of the former compound is reproduced in Fig. 1. The two singlets at δ 1.26 and at 1.61 ppm may be assigned to the methyl protons and arise from the *trans*-geometry of the complex. The double-doublets centred at δ 6.22 and at 6.7–7.0 ppm, (J 8, 8 Hz) and the downfield doublets at δ 7.00 and 7.50 ppm (J 8.0 Hz) may be assigned to H_B, H_C, H_A and H_D protons, respectively, arising from coupling to neighbouring protons (chemically equivalent but magnetically non-equivalent) [20] of the C_5H_4 moiety in the complex. Similar type of splitting was reported previously for other $\eta^1:\eta^5$-cyclopentadienyl bridged complexes [21,22]. A multiplet centred at δ 6.7–6.9 ppm may be due to the phenyl protons. A pair of downfield doublets (broad) at δ 7.70 ppm (J 8 Hz) and at δ 7.80 ppm (J 8 Hz) typical of *p*-substituted phenyl ring may be assigned to the protons of the *p*-ClC_6H_4 group. Thus, the high field PMR confirms the structure in which two titanium atoms are bridged through $\eta^1:\eta^5$-cyclopentadienylidene groups, giving rise to the presence of both Ti–C(σ) and Ti–C(π) bonds.

The transformation of (η^5-C_5H_5)M species to M-($\eta^5:\eta^1$-C_5H_4)M and M-($\eta^5:\eta^1$-$C_{10}H_8$)M type of systems has now been recognized as an important aspect of the organotransition metal chemistry [22,23–27], and the abstraction of hydrogen from the cyclopentadienyl ring in titanocene possibly takes place via a (η^1-C_5H_5) system [23]. Monohapto:pentahapto bonding in Cp-bridging compounds has been described previously [28–31].

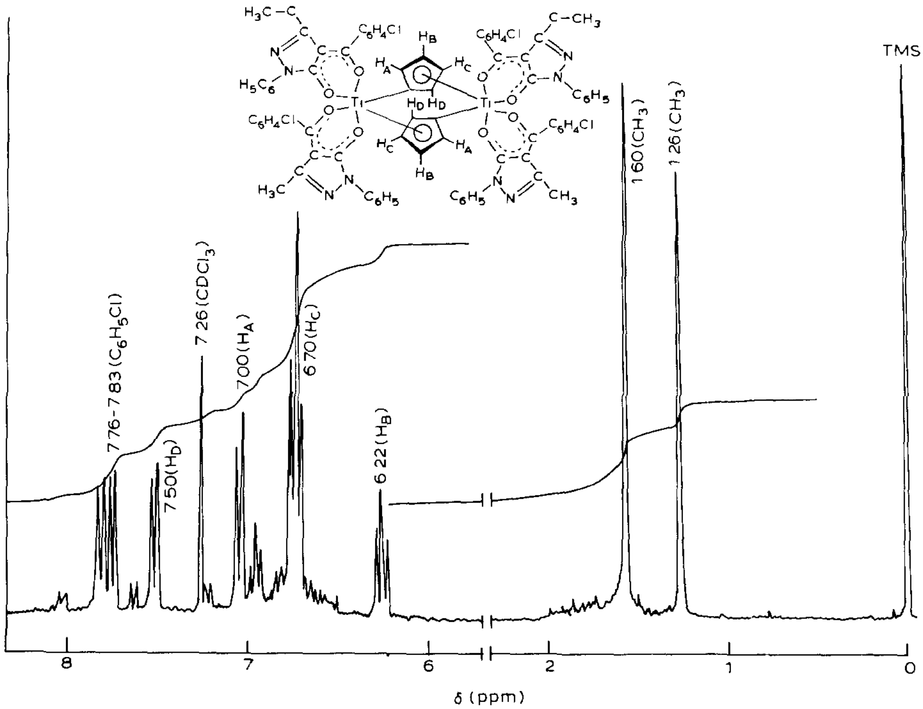
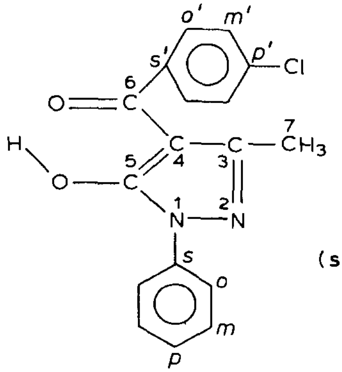


Fig. 1. ^{1}H NMR spectrum (270 MHz, rel. to TMS) of structure III.

^{13}C NMR spectra

A comparison of the ^{13}C NMR spectrum of the ligand, CMPPOH, (IV) with the



(s = s′ = substituted carbon)

(IV)

corresponding cyclopentadienyl complex, (η^1 : η^5-cyclopentadienyl)bis-(4-*p*-chlorobenzoyl-3-methyl-1-phenyl-2-pyrazolin-5-onato)titanium(IV), gave useful information, as follows:

(1) A downfield shift was observed for the C(4) and C(5) signals but an upfield shift for C(6). This is probably due to a quasi-aromatic nature of the ring in this complex, involving, C(4), C(5), C(6) and the two oxygen atoms to form a system of the type $O \overset{...}{-} \underset{6}{C} \overset{...}{-} \underset{4}{C} \overset{...}{-} \underset{5}{C} \overset{...}{-} O$. The delocalization of electrons in the ring during the complex

(Continued on p. 308)

TABLE 1

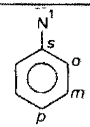
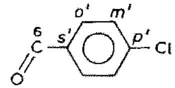
REACTIONS OF DICYCLOPENTADIENYLTITANIUM(IV) DICHLORIDE AND MONOCYCLOPENTADIENYLTITANIUM TRICHLORIDE WITH 4-ACYL-3-METHYL-1-PHENYL-2-PYRAZOLIN-5-ONES

Reactants			Product	MW	$Et_3N \cdot HCl$	Analyses (Found (calcd.) (%))			
$(C_5H_5)_2TiCl_2$ (g)	Pyrazolone (g)	Et_3N (g)	(Yield (%))	Found (calcd.)	Found (calcd.) (g)	Ti	Cl	C	H
	A		$(C_5H_5)_2TiCl(A)$	510	0.91	9.70	7.09	65.98	4.60
1.84	2.05	0.75	(50)	(490)	(1.01)	(9.76)	(7.22)	(66.06)	(4.68)
	A		$[(C_5H_4)TiA_2]_2$	1290	1.39	7.10	–	70.15	4.40
1.33	2.97	1.08	(55)	(666)	(1.47)	(7.19)		(70.27)	(4.50)
	B		$(C_5H_5)_2TiCl(B)$	450	1.00	10.79	7.80	62.00	5.13
2.01	1.86	0.82	(52)	(442)	(1.11)	(10.82)	(8.01)	(62.36)	(5.19)
	B		$[(C_5H_4)TiB_2]_2$	1165	2.00	8.30	–	65.10	5.15
1.93	3.58	1.57	(51)	(570)	(2.14)	(8.40)		(65.24)	(5.26)
	C		$(C_5H_5)_2TiCl(C)$	–	0.95	11.16	8.09	–	–
1.76	1.53	0.72	(58)		(0.98)	(11.17)	(8.27)		
	C		$[(C_5H_4)TiC_2]_2$	1050	1.49	8.75	–	–	–
1.39	2.42	1.13	(57)	(542)	(1.54)	(8.83)			
	D		$(C_5H_5)_2TiCl(D)$	–	0.81	9.09	6.45	–	–
1.49	1.88	0.60	(57)		(0.82)	(9.12)	(6.75)		
	D		$[(C_5H_4)TiD_2]_2$	–	1.00	6.49	–	–	–
1.00	2.52	0.81	(58)		(1.11)	(6.52)			
$C_5H_5TiCl_3$	A		$(C_5H_5)TiCl(A)_2$	–	1.00	6.78	4.69	–	–
1.16	2.96	1.07	(55)		(1.07)	(6.82)	(5.04)		
$C_5H_5TiCl(A)_2$	–		$[(C_5H_4)TiA_2]_2$	1280	0.15	7.09	–	63.55	3.70
0.91		0.13	(56)	(666)	(0.17)	(7.12)		(63.68)	(3.81)

[a] A = 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one, B = 4-Propionyl-3-methyl-1-phenyl-2-pyrazolin-5-one; C = 4-Acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one, D = 4-Chlorobenzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one.

TABLE 2

^{13}C NMR DATA FOR 4-*p*-CHLOROBENZOYL-3-METHYL-1-PHENYL-2-PYRAZOLIN-5-ONE AND THE CORRESPONDING CYCLOPENTADIENYLTITANIUM COMPLEX (δ (ppm) rel. to TMS)

Ligand/Complex	C(7) (CH_3)	C(4)	C(3)	C(5)	C(6)							C_5H_4	
						m	*p*	*o*	*s*	*m'*	*o'*	*p'*	*s'*
L [a]	15.81	103.20	137.36	161.39	190.68	120.87	128.77	129.11	147.59	126.76	129.46	136.21 138.23	–
$[(C_5H_4)TiL_2]_2$	16.12	107.54	137.55	162.69	188.68	119.75	127.63	128.65	148.71	125.21	128.84	136.82 138.02	129.73 131.97
	16.46	107.69	137.14	164.46	188.67				148.58				133.76

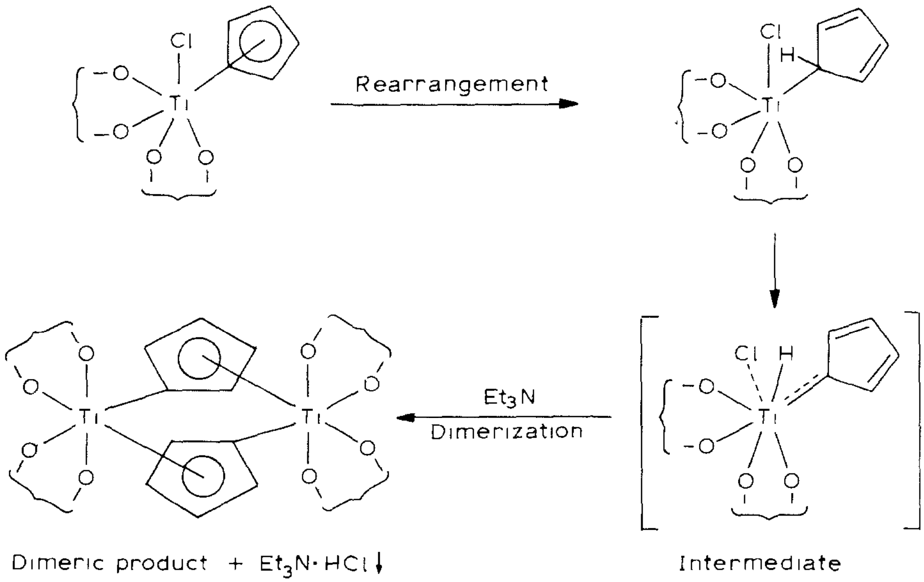
[a] Where L is 4-*p*-chlorobenzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one.

formation changes the chemical shift for the carbon atoms.

(2) The splitting of almost all the carbon signals into two may be due to the presence of the ligand species in *trans*-geometry.

(3) Three new signals (singlets) at δ 133.74, 131.97 and 129.73 ppm can be assigned to C(1), C(2) and C(3) of the C_5H_4 moiety (C(2) and C(2′), C(3) and C(3′) are magnetically equivalent). The appearance of these three signals in the ^{13}C NMR spectrum further confirms the presence of $\eta^1 : \eta^5$-bonding [27] in the complex.

The formation of bis-derivatives, $[(C_5H_4)TiL_2]_2$, can be accounted for in terms of the following rearrangement.



SCHEME 1

In this rearrangement, one of the ring hydrogens moves to the η^1-position and subsequently shifts to the titanium centre, and then in the presence of Et_3N is removed as $Et_3N \cdot HCl$.

Experimental

Synthesis of complexes

Titanocene dichloride (1.84 g, 7.39 mmol) was suspended in dry THF and the ligand (BMPPOH) solution (2.05 g, 7.39 mmol) and triethylamine (0.75 g, 7.41 mmol) was added. The mixture gradually turned black with the evolution of heat. It was subsequently refluxed for ~ 3–4 h, then the $Et_3N \cdot HCl$ was filtered off. The filtrate was evaporated under reduced pressure to leave a black-red solid, which was recrystallized from benzene/petroleum ether mixture. Some physical constants and the analyses of the new complexes are listed in Table 1. All solvents were dried before use. All manipulations were carried out under strictly anhydrous conditions. Cp_2TiCl_2 was recrystallized from hot toluene solution. The ligands were made as reported earlier [32]. Titanium was estimated as TiO_2 [33] and chlorine by Volhard's method [34].

Physical measurements

Molecular weights were determined in a semi-micro ebulliometer (Gallenkamp) equipped with a thermister sensor. Infrared spectra were recorded in Nujol on a Perkin–Elmer 577 grating spectrophotometer using cesium iodide optics. Proton NMR (270 MHz) were recorded in $CDCl_3$ (Table 2) at the Bangalore. NMR facility, Indian Institute of Sciences, Bangalore.

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