Journal of Organometallic Chemistry, 332 (1987) 135–139
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Some new organozirconium(IV) compounds with *N*-(aryl)-2-mercaptoacetamides

Satish C. Dixit, Ram Sharan, and Ramesh N. Kapoor *

Department of Chemistry, University of Delhi, Delhi-110007 (India)

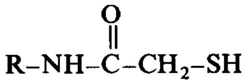
(Received February 25th, 1987)

Abstract

Reactions of dichlorodicyclopentadienylzirconium(IV) with various stoichiometric proportions of mercaptoacetamides have been examined. Complexes of the type $Cp_2Zr(MA)Cl$ and $Cp_2Zr(MA)_2$ (Cp = Cyclopentadienyl and MAH = *N*-(aryl)-2-mercaptoacetamide; aryl = phenyl, *o*-tolyl, *m*-tolyl, *p*-tolyl, α-naphthyl or 3,5-dimethylphenyl) were obtained, and were characterized by elemental analysis and by ^1H NMR, variable temperature ^1H NMR, IR, and electronic spectral data.

Introduction

There has been an enormous upsurge of interest in the chemistry of transition metal complexes containing nitrogen-oxygen-sulphur chelating ligands [1,2]. This may be attributed to the reported carcinostatic and antiviral activity of several such ligands and their complexes [3–5]. We describe here the results of a study of the reactions of Cp_2ZrCl_2 with various mercaptoacetamides aimed at investigation of the possible coordination sites of ligands in the complexes. The mercaptoacetamides used were as follows:



$$R\text{-}NH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}SH$$

R = phenyl (PMAH), R = *o*-tolyl (*o*-TMAH), R = *m*-tolyl (*m*-TMAH), R = *p*-tolyl (*p*-TMAH), R = α-naphthyl (NMAH), R = 3,5-dimethylphenyl (DMPH).

Results and discussion

The reaction of dichlorodicyclopentadienylzirconium(IV) with *N*-(aryl)-2-mercaptoacetamides in 1/1 and 1/2 molar ratio in anhydrous THF in the presence

0022-328X/87/$03.50

of triethylamine are represented by the following equations (where MA^- represents the anion of the corresponding bidentate mercaptoacetamide, MAH):

$$Cp_2ZrCl_2 + MAH + Et_3N \xrightarrow[\text{room temp.}]{\text{THF}} Cp_2Zr(MA)Cl + Et_3N \cdot HCl$$

$$Cp_2ZrCl_2 + 2MAH + 2Et_3N \xrightarrow[\text{room temp.}]{\text{THF}} Cp_2Zr(MA)_2 + 2Et_3N \cdot HCl$$

All the complexes are crystalline, and extremely sensitive to hydrolysis. These are soluble in tetrahydrofuran and chloroform, but insoluble in n-hexane and petroleum ether.

The IR spectra of the complexes show the usual absorptions due to cyclopentadienyl groups at ~ 3100 cm^{-1} (ν(C–H)), ~ 1435 cm^{-1} (ν(C–C)), ~ 1020 cm^{-1} ($\delta_{i.p.}$(CH)) and ~ 810 cm^{-1} ($\delta_{o.p.}$(CH)) [10]. The persistence of the bands of cyclopentadienyl rings in the complexes indicate that these groups are π-bonded to the metal and retain their aromatic character. The IR spectra of the ligands show a medium intensity band in the region 3280–3240 cm^{-1} which is assigned to ν(NH) [11]. The complexes give a ν(NH) band in almost the same region, which suggests that the amide group nitrogen is not involved in the coordination to the metal. Mercaptoacetamides show a weak band in the region 2560–2500 cm^{-1}, attributable to ν(SH) [12] and disappearance of this band in the spectra of the complexes indicates the deprotonation of thiol-*S*. The ligands show medium to strong bands in the regions 1645–1640, 1545–1530, 1280–1270, 720–685 and 610–590 cm^{-1} which may be assigned to amide-I (ν(C=O)), amide-II (ν(CN) + δ(NH)), amide-III (ν(CN) + δ(NH)), amide-V ($\delta_{o.p.}$(C=O)), and amide-IV ($\delta_{i.p.}$(C=O)), respectively [13]. In the complexes amide-I, the ν(C=O) band appears at lower frequencies (1630–1600 cm^{-1}); this downward shift indicates a decrease in the carbon–oxygen bond order and coordination of the carbonyl oxygen of the amide group to the metal. However, there are other amide bands in almost the same region, which confirms that the amide nitrogen does not participate in the coordination. The band at ~ 450 cm^{-1} can be assigned to ν(Zr–O) [14].

^1H NMR spectra (see Table 2) of all the complexes show a signal due to cyclopentadienyl groups at ~ δ 6.3 ppm [15,16]. The ^1H NMR spectra of the mercaptoacetamides recorded in deuterated chloroform show a triplet in the region δ 2.2–1.9 ppm due to the SH proton, but this signal is absent for the corresponding zirconium complexes, which confirms the deprotonation of the ligands in the complexes. The appearance of a singlet from the NH proton in the same region δ 8.3–8.0 ppm, for both of the ligands as well as for the complexes, shows again that the nitrogen is not involved in bonding. The integrated proton ratios were as expected for the formulae assigned to the complexes.

Variable temperature (−50 to +50 °C) ^1H NMR spectra recorded for a representative of each of the two classes of compounds show only a singlet for the methylene protons at all temperatures.

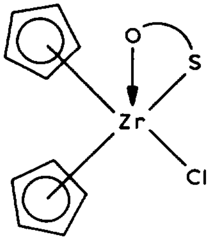
The electronic spectra of all the complexes were recorded with chloroform solutions and the data are shown in Table 1. The fairly intense bands between 294 nm and 247 nm can be assigned to a charge transfer band [17], and is in accord with the $(n-1)d^0$, ns^0 electronic configurations of the complexes.

Table 1

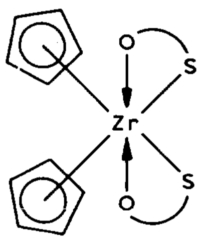
Characterisation data

Complex	M.P. (°C)	Colour	Analysis (Found (Calcd.) (%))					λ_{max} (nm) (in $CHCl_3$)
			Zr	C	H	N	Cl	
$(C_5H_5)_2Zr(m\text{-TMA})Cl$	110	Grey	20.78 (20.89)	52.04 (52.21)	–	3.9 (3.21)	8.08 (8.13)	250.8
$(C_5H_5)_2Zr(m\text{-TMA})_2$	125	Dark Grey	15.53 (15.69)	–	–	4.64 (4.82)	–	259.8
$(C_5H_5)_2Zr(p\text{-TMA})Cl$	145	Light Orange	20.61 (20.89)	–	4.08 (4.58)	–	8.06 (8.13)	255.6
$(C_5H_5)_2Zr(p\text{-TMA})_2$	143	Light Brown	15.71 (15.69)	57.4 (57.81)	5.26 (5.16)	–	–	254.8
$(C_5H_5)_2Zr(o\text{-TMA})Cl$	115	Yellowish Brown	20.77 (20.89)	–	–	–	8.02 (8.13)	255.8
$(C_5H_5)_2Zr(o\text{-TMA})_2$	138	Yellowish Brown	15.64 (15.69)	–	–	4.38 (4.82)	–	257.0
$(C_5H_5)_2Zr(PMA)Cl$	110	Chocolate	21.1 (21.58)	–	4.0 (4.26)	3.54 (3.31)	8.18 (8.40)	247.2
$(C_5H_5)_2Zr(PMA)_2$	110	Cream	16.29 (16.49)	57.04 (56.4)	4.16 (4.7)	5.08 (5.06)	–	253.2
$(C_5H_5)_2Zr(NMA)Cl$	178	Light chocolate	19.03 (19.30)	–	–	–	7.43 (7.51)	282.4
$(C_5H_5)_2Zr(NMA)_2$	160	Cream	13.86 (13.96)	59.23 (62.46)	4.47 (4.59)	4.88 (4.29)	–	294.0
$(C_5H_5)_2Zr(DMP)Cl$	180	Light Brown	20.18 (20.24)	–	–	–	7.8 (7.88)	253.2
$(C_5H_5)_2Zr(DMP)_2$	205	Cream	14.88 (14.97)	61.13 (59.09)	–	4.44 (4.60)	–	256.0

From the elemental analyses and spectral data, it appears that mercaptoacetamides behave as monofunctional bidentate (O,S) chelating ligands. The penta- and hexa-coordinated structures **A** and **B** are tentatively proposed for the complexes of the type $Cp_2Zr(MA)Cl$ (**A**) and $Cp_2Zr(MA)_2$ (**B**):



(A)



(B)

= anion of bidentate mercaptoacetamide

Cotton et al. [18] showed by crystallographic studies that in $(C_5H_5)_4Ti$ two cyclopentadienyl rings are pentahapto and the remaining two monohapto, thus giving a 16 electron system. In the case of $Zr(C_5H_5)_4$ Cotton et al. concluded one cyclopentadienyl ring is monohapto, one ring pentahapto, and the other two rings act as 4-electron donors, leading to an 18-electron system, this conflicts with the view of Kulishov et al. [19,20], who suggested that in $Zr(C_5H_5)_4$ there are three pentahapto-cyclopentadienyl rings with the fourth ring monohapto, leading to a 20-electron system. We suggest by analogy with the conclusion of Cotton et al. [18], that in the complexes $Cp_2Zr(MA)_2$, one cyclopentadienyl ring is pentahapto and the other ring is a 3-electron donor, leading to an 18-electron system.

Experimental

Sodium cyclopentadienide and dicyclopentadienylzirconium(IV) chloride were prepared by standard methods [6,7]. THF (Ferak, Berlin, West Germany) was dried by storage over sodium wire overnight and then refluxed until it gave a blue colour with benzophenone, and then was distilled from $LiAlH_4$. n-Hexane and triethylamine were dried by standard methods [8]. Mercaptoacetamides were synthesized by condensation of thioglycollic acid with the appropriate arylamines [9]. Stringent precautions were taken to exclude moisture from the system and reactions were carried out under dry nitrogen with the system well-protected from atmospheric moisture by means of $CaCl_2$ guard tubes.

Zirconium was estimated gravimetrically as ZrO_2. Analysis for carbon, hydrogen and nitrogen were carried out at the central Micro-Anaytical Laboratory of the Indian Institute of Technology, Kanpur. Chlorine was determined as AgCl. The IR spectra were recorded in KBr pellets on a Shimadzu IR-435 spectrophotometer in the region 4000–400 cm^{-1}. The ^1H NMR spectra (Table 2) were recorded on a JEOL-JNM-FX200 Fourier Transform spectrometer with $CDCl_3$ as solvent. The electronic spectra of the complexes in chloroform were recorded on a Shimadzu UV-260 spectrophotometer.

Table 2

Proton chemical shifts (δ, ppm) at room temperature

Compound	C_5H_5	Aromatic ring	NH	CH_3	CH_2
$(C_5H_5)_2Zr(m\text{-TMA})Cl$	6.32	7.4m	8.30s	2.32s	3.67s
$(C_5H_5)_2Zr(m\text{-TMA})_2$	6.56	7.32m	8.29s	2.36s	3.68s
$(C_5H_5)_2Zr(p\text{-TMA})Cl$	6.56	7.32m	8.24s	2.32s	3.68s
$(C_5H_5)_2Zr(p\text{-TMA})_2$	6.56	7.32m	8.28s	2.36s	3.68s
$(C_5H_5)_2Zr(o\text{-TMA})Cl$	6.32	7.4m	8.30s	2.36s	3.8s
$(C_5H_5)_2Zr(o\text{-TMA})_2$	6.56	7.32m	8.28s	2.28s	3.76s
$(C_5H_5)_2Zr(PMA)Cl$	6.6	7.4m	8.0s	–	3.76s
$(C_5H_5)_2Zr(PMA)_2$	6.29	7.4m	8.08s	–	3.76s
$(C_5H_5)_2Zr(NMA)Cl$	6.36	7.32m	8.30s	–	3.92s
$(C_5H_5)_2Zr(NMA)_2$	6.5	7.6m	8.24s	–	3.96s
$(C_5H_5)_2Zr(DMP)Cl$	6.32	7.32m	8.28s	2.32s	3.68s
$(C_5H_5)_2Zr(DMP)_2$	6.52	7.32m	8.30s	2.28s	3.64s

Synthesis of complexes

Reaction of dichlorodicyclopentadienylzirconium(IV) (1 mol) with N-(aryl)-2-mercaptoacetamide (1 mol). A general procedure was followed to synthesize these complexes. To the solution of Cp_2ZrCl_2 (0.48 g, 1.64 mmol; 0.71 g, 2.43 mmol) in dry tetrahydrofuran (~ 80 ml) was added *N*-(aryl)-2-mercaptoacetamide (0.30 g, 1.66 mmol; 0.53 g, 2.44 mmol) and triethylamine (0.17 g, 1.68 mmol; 0.25 g, 2.47 mmol). The mixture was stirred for ~ 60 h at room temperature then precipitated $Et_3N \cdot HCl$ was filtered off, and the solvent was removed in vacuo. The solids obtained were recrystallised from a n-hexane/THF mixture. Details of the complexes are given in Table 1.

Reaction of dichlorodicyclopentadienylzirconium(IV) (1 mol) with N-(aryl)-2-mercaptoacetamide (2 mol). A common procedure was used for synthesis of all the complexes. To a solution of Cp_2ZrCl_2 (0.15 g, 0.51 mmol; 0.56 g, 1.92 mmol) and *N*-(aryl)-2-mercaptoacetamide (0.11 g, 0.51 mmol; 0.69 g, 3.81 mmol) in dry THF (~ 80 ml) was added triethylamine (0.10 g, 0.99 mmol; 0.39 g, 3.85 mmol). The subsequent procedure was as described above. Details of the complexes obtained are given in Table 1.

Acknowledgement

One of the authors (SCD) thanks the University Grants Commission, New Delhi for the award of a Teacher Fellowship.

References

1 M. Akbar Ali, S.E. Livingstone and D.J. Phillips, Inorg. Chim. Acta, 7 (1973) 179.
2 M. Das and S.E. Livingstone, Inorg. Chim. Acta, 19 (1976) 5.
3 M. Akbar Ali and S.E. Livingstone, Coord. Chem. Rev., 13 (1974) 101.
4 M.J. Cleare, Coord. Chem. Rev., 12 (1974) 349.
5 O.P. Pandey, S.K. Sengupta and S.C. Tripathi, Synth. React. Inorg. Met.-Org. Chem., 13 (1983) 867.
6 W.L. Jolly, Synthetic Inorganic Chemistry, Prentice-Hall of India (Pvt.) Ltd., New Delhi, 1965, p. 176.
7 G. Wilkinson and J.M. Birmingham, J. Am. Chem. Soc., 76 (1954) 4281.
8 A.I. Vogel, A Textbook of Practical Organic Chemistry, Longman Green, London, 1948.
9 R.N. Mishra and S.S. Guha Sirkar, J. Indian Chem. Soc., 32 (1955) 127.
10 H.P. Fritz, Advan. Organomet. Chem., 1 (1964) 262.
11 K. Nag and D.S. Joardar, Inorg. Chim. Acta, 14 (1975) 133.
12 M. Chaudhury, J. Chem. Soc. Dalton Trans., (1984) 115.
13 L.J. Bellamy, The Infrared Spectra of Complex Molecules, Chapman and Hall, London, 1975.
14 K.C. Malhotra and S.C. Chaudhary, Austral. J. Chem., 27 (1974) 79.
15 P.C. Wailes, H. Weigold and A.P. Bell, J. Organomet. Chem., 33 (1971) 181.
16 E. Samuel, Bull. Soc. Chim. Fr., (1966) 3548.
17 P.B. Dorain, H.H. Patterson and P.C. Jordon, J. Chem. Phys., 49 (1968) 3845.
18 F.A. Cotton, J.L. Calderon, B.G. Deboer and J. Takats, J. Am. Chem. Soc., 93 (1971) 3592.
19 V.I. Kulishov, N.G. Bokii and Yu.T. Struchkov, Zh. Strukt. Khim., 11 (1970) 700.
20 V.I. Kulishov, E.M. Brainina, N.G. Bokiy and Yu.T. Struchkov, Chem. Commun., (1970) 475.