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ALIPHATIC ACID DIHYDRAZIDE DERIVATIVES OF DICYCLOPENTADIENYLZIRCONIUM(IV) DICHLORIDE AND THEIR REACTIONS WITH β-DIKETONES. FORMATION OF CYCLIC COMPOUNDS

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Summary

The reactions of dicyclopentadienylzirconium(IV) dichloride with bidentate aliphatic acid dihydrazide (LH_2) derived from oxalic, succinic, and adipic acids (metal to ligand molar ratios 1 : 1 and 1 : 2, respectively) in anhydrous tetrahydrofuran in the presence of base led to the formation of the $[Cp_2Zr(L)]$ and $[CpZr(LH)_2Cl]$ complexes. The complexes were characterized by elemental analyses, electrical conductance, magnetic measurements and spectroscopic studies. These ligands appear to behave as bidentate chelate agents. All the complexes contain terminal amino or terminal hydrazinic nitrogen atoms with an unshared electron pair, enabling nucleophilic condensations. Therefore, the reactions of these complexes with β-diketones (acetylacetone, benzoylacetone, dibenzoylmethane, thenoyltrifluoroacetone) in the presence of glacial acetic acid have been studied viz., ring closure and formation of macrocyclic ligand (mac) complexes. Two types of cyclic products viz., $[Cp_2Zr(mac)]$ and $[CpZr(mac)Cl]$ were isolated. The spectral studies of these cyclic products are reported.

Introduction

The transition metal complexes of some aliphatic and aromatic acid dihydrazides have been reported [1–6]. Hydrazides have been found to act as bidentate ligands with coordination sites either at two amide oxygen atoms, or at two deprotonated amide nitrogen atoms. However, no paper has been published on the cyclization of acid dihydrazides by the metal template effect to yield macrocyclic compounds. The intense interest in synthetic macrocycles and their metal complexes depends on the fact that they mimic naturally occurring macrocyclic molecules in their structural and functional features and their rich chemical behaviour [7,8]. The formation of macrocyclic complexes strongly depends on the dimensions of the internal cavity,

(*Continued on p. 30*)

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TABLE 1. ALIPHATIC ACID DIHYDRAZIDE DERIVATIVES OF ZIRCONIUM(IV) AND THEIR REACTIONS WITH β-DIKETONES

Reactants [a] (molar ratio)	Stirring/ refluxing time (h)	Product, colour, yield (%)	Decomp. temp. (°C)	Analysis (Found (calc) (%))				
				C	H	N	Zr	Cl
$Cp_2ZrCl_2 + ODH_2 + Et_3N$ (1:1:2)	40	$[Cp_2Zr(OD)]$, cream, 68	208	42.6 (42.7)	4.1 (4.1)	16.4 (16.6)	27.0 (27.0)	–
$Cp_2ZrCl_2 + SDH_2 + Et_3N$ (1:1:2)	50	$[Cp_2Zr(SD)]$, light brown, 62	112	45.9 (45.9)	4.8 (4.9)	15.2 (15.3)	24.9 (24.9)	–
$Cp_2ZrCl_2 + ADH_2 + Et_3N$ (1:1:2)	50	$[Cp_2Zr(Ad)]$, brown, 59	245	48.7 (48.8)	5.5 (5.5)	14.2 (14.2)	23.1 (23.1)	—
$Cp_2ZrCl_2 + ODH_2 + BuNH_2$ (1:2:1)	50	$[CpZr(ODH)_2Cl]$, light yellow, 70	269	25.1 (25.3)	3.5 (3.5)	26.2 (26.3)	21.4 (21.4)	8.3 (8.3)
$Cp_2ZrCl_2 + SDH_2 + BuNH_2$ (1:2:1)	55	$[CpZr(SDH)_2Cl]$, brown, 61	225	32.3 (32.3)	4.7 (4.7)	23.1 (23.2)	18.8 (18.9)	7.3 (7.3)
$Cp_2ZrCl_2 + ADH_2 + BuNH_2$ (1:2:1)	60	$[CpZr(ADH)_2Cl]$, light yellow, 60	210	37.9 (37.9)	5.6 (5.7)	20.7 (20.8)	16.9 (16.9)	6.6 (6.6)
$Cp_2Zr(OD)$ + acac (1:1)	16	$[Cp_2Zr(mac(1))]$, light brown, 54	220	50.8 (50.8)	4.3 (4.4)	13.8 (13.9)	22.7 (22.7)	–
$Cp_2Zr(OD)$ + bzac (1:1)	18	$[Cp_2Zr(mac(2))]$, brown, 60	195	56.7 (56.9)	4.2 (4.3)	12.0 (12.0)	19.6 (19.6)	–
$Cp_2Zr(OD)$ + dbm (1:1)	20	$[Cp_2Zr(mac(3))]$, brown, 52	248	61.6 (61.6)	4.0 (4.1)	10.6 (10.6)	17.2 (17.3)	–
$[Cp_2Zr(OD)]$ + tfac	25	$[Cp_2Zr(mac(4))]$, light yellow, 50	292	45.8 (45.8)	2.7 (2.8)	10.6 (10.7)	17.4 (17.4)	–
$[Cp_2Zr(SD)]$ + acac (1:1)	20	$[Cp_2Zr(mac(5))]$, dark brown, 48	234	53.0 (53.1)	5.0 (5.1)	13.0 (13.0)	21.2 (21.2)	–
$[Cp_2Zr(SD)]$ + bzac (1:1)	20	$[Cp_2Zr(mac(6))]$, yellowish brown, 52	210	58.6 (58.6)	4.8 (4.8)	11.3 (11.4)	18.4 (18.5)	–
$[Cp_2Zr(SD)]$ + dbm (1:1)	22	$[Cp_2Zr(mac(7))]$, dark brown, 50	200	62.9 (62.9)	4.5 (4.6)	10.0 (10.1)	16.4 (16.4)	–
$[Cp_2Zr(SD)]$ + tfac (1:1)	25	$[Cp_2Zr(mac(8))]$, light brown, 56	186	47.8 (47.8)	3.4 (3.4)	10.1 (10.1)	16.5 (16.5)	
$[Cp_2Zr(AD)]$ + acac (1:1)	18	$[Cp_2Zr(mac(9))]$, brown, 50	154	55.0 (55.1)	5.5 (5.6)	12.2 (12.2)	19.9 (19.9)	–
$[Cp_2Zr(AD)]$ + bzac (1:1)	18	$[Cp_2Zr(mac(10))]$, brown, 45	189	60.0 (60.0)	5.1 (5.3)	10.7 (10.7)	17.5 (17.5)	–
$[Cp_2Zr(AD)]$ + dbm (1:1)	22	$[Cp_2Zr(mac(11))]$, yellow, 55	260	64.0 (64.0)	5.0 (5.1)	9.5 (9.6)	15.6 (15.6)	–

$[Cp_2Zr(AD)]$ + tfac (1 : 1)	25	$[Cp_2Zr(mac(12))]$, orange-yellow, 48	152	49.7 (49.7)	3.9 (3.9)	9.5 (9.6)	15.7 (15.7)	–
$[CpZr(ODH)_2Cl]$ + acac (1 : 1)	20	[CpZr(mac(13))Cl], brown, 65	300	38.5 (38.7)	3.4 (3.4)	15.0 (15.0)	24.3 (24.5)	9.5 (9.5)
$[CpZr(ODH)_2Cl]$ + bzac (1 : 1)	25	[CpZr(mac(14))Cl], orange brown, 60	220	47.0 (47.0)	3.2 (3.4)	12.8 (12.9)	21.0 (21.0)	8.1 (8.1)
$[CpZr(ODH)_2Cl]$ + dbm (1 : 1)	28	[CpZr(mac(15))Cl], yellow, 68	189	53.0 (53.2)	3.3 (3.4)	11.1 (11.2)	18.4 (18.4)	7.0 (7.1)
$[CpZr(ODH)_2Cl]$ + tfac (1 : 1)	28	[CpZr(mac(16))Cl], dark brown, 70	270	36.4 (36.4)	2.0 (2.0)	11.2 (11.3)	18.3 (18.4)	7.1 (7.1)
$[CpZr(SDH)_2Cl]$ + acac (1 : 1)	25	[CpZr(mac(17))Cl], yellowish orange, 58	200	41.9 (42.0)	4.2 (4.2)	14.0 (14.0)	22.8 (22.8)	8.7 (8.8)
$[CpZr(SDH)_2Cl]$ + bzac (1 : 1)	25	[CpZr(mac(18))Cl], Orange, 55	180	49.3 (49.3)	4.0 (4.1)	12.0 (12.1)	19.7 (19.7)	7.6 (7.6)
$[CpZr(SDH)_2Cl]$ + dbm (1 : 1)	30	[CpZr(mac(19))Cl], dark yellow, 60	140	54.8 (54.9)	4.0 (4.0)	10.6 (10.6)	7.2 (7.4)	6.6 (6.7)
$[CpZr(SDH)_2Cl]$ + tfac (1 : 1)	32	[CpZr(mac(20))Cl], dark brown, 68	270	39.0 (39.1)	2.6 (2.6)	10.7 (10.7)	17.4 (17.4)	6.8 (6.8)
$[CpZr(ADH)_2Cl]$ + Acac (1 : 1)	28	[CpZr(mac(21))Cl], chocolate, 68	285	44.8 (44.8)	4.7 (4.9)	13.0 (13.0)	21.2 (21.3)	8.2 (8.2)
$[CpZr(ADH)_2Cl]$ + bzac (1 : 1)	30	[CpZr(mac(22))Cl], yellowish brown, 60	262	51.3 (51.4)	4.6 (4.6)	11.3 (11.4)	18.6 (18.6)	7.2 (7.2)
$[CpZr(ADH)_2Cl]$ + dbm (1 : 1)	32	[CpZr(mac(23))Cl], dark brown, 62	146	56.4 (56.5)	4.3 (4.5)	10.1 (10.1)	16.5 (16.5)	6.4 (6.4)
$[CpZr(ADH)_2Cl]$ + tfac (1 : 1)	32	[CpZr(mac(24))Cl], dark brown, 70	182	41.3 (41.4)	3.1 (3.2)	10.1 (10.1)	16.5 (16.5)	6.4 (6.4)

[a] ODH_2 = oxalic acid dihydrazide; SDH_2 = succinic acid dihydrazide; ADH_2 = adipic acid dihydrazide; acac = acetylacetone; bzac = benzoylacetone; dbm = dibenzoylmethane; tfac = thenoyltrifluoroacetone; mac(1) = macrocyclic ligand derived from acetylacetone; mac(2) = macrocyclic ligand derived from benzoylacetone; mac(3) = macrocyclic ligand derived from dibenzoylmethane; mac(4) = macrocyclic ligand derived from thenoyltrifluoroacetone; mac(5) = macrocyclic ligand derived from acetylacetone; mac(6) = macrocyclic ligand derived from benzoylacetone; mac(7) = macrocyclic ligand derived from dibenzoylmethane; mac(8) = macrocyclic ligand derived from thenoyltrifluoroacetone; mac(9) = macrocyclic ligand derived from acetylacetone; mac(10) = macrocyclic ligand derived from benzoylacetone; mac(11) = macrocyclic ligand derived from dibenzoylmethane; mac(12) = macrocyclic ligand derived from thenoyltrifluoroacetone; mac(13) = macrocyclic ligand derived from acetylacetone; mac(14) = macrocyclic ligand derived from benzoylacetone; mac(15) = macrocyclic ligand derived from dibenzoylmethane; mac(16) = macrocyclic ligand derived from thenoyltrifluoroacetone; mac(17) = macrocyclic ligand derived from acetylacetone; mac(18) = macrocyclic ligand derived from benzoylacetone; mac(19) = macrocyclic ligand derived from dibenzoylmethane; mac(20) = macrocyclic ligand derived from thenoyltrifluoroacetone; mac(21) = macrocyclic ligand derived from acetylacetone; mac(22) = macrocyclic ligand derived from benzoylacetone; mac(23) = macrocyclic ligand derived from dibenzoylmethane; mac(24) = macrocyclic ligand derived from thenoyltrifluoroacetone.

the rigidity of the macrocycle, the nature of its donor atoms and the complexing properties of the anions involved in the coordination [9,10]. The synthesis of macrocyclic compounds is generally carried out in the presence of a suitable salt, the cation of which is assumed to act as a template for ring formation [7,11]. Here, we report the template behaviour of dicyclopentadienylzirconium(IV) towards the cyclization of acid dihydrazides by β-diketones. This is the first report on template behaviour of an organozirconium species.

Experimental

The chemicals used were British Drug House products. All the reactions were carried out under strictly anhydrous conditions. Tetrahydrofuran was dried on sodium wire overnight and then refluxed until it gave a blue colour with benzophenone. Benzene was refluxed over sodium wire overnight and then distilled. All traces of moisture were azeotropically removed with ethanol and fractionated. Triethylamine and n-butylamine were purified by a published method [12]. Dicyclopentadienylzirconium(IV) dichloride was prepared by treatment of sodium cyclopentadienide and zirconium(IV) chloride in a nitrogen atmosphere [13]. The dihydrazides were synthesized by the method of Bülow and Weidlich [14].

Elemental analyses and physical measurements were made as described earlier [15].

(A) Reactions of Cp_2ZrCl_2 with dihydrazides (molar ratio 1 : 1)

A mixture of Cp_2ZrCl_2 (10 mmol), the appropriate dihydrazide (10 mmol) and triethylamine (20 mmol) was stirred in dry tetrahydrofuran (60 ml) for 40–50 h at room temperature. The reaction mixture was filtered to remove triethylamine hydrochloride and the clear filtrate was evaporated to dryness under reduced pressure. The complex was recrystallised from a THF/petroleum ether mixture.

(B) Reactions of Cp_2ZrCl_2 with dihydrazides (molar ratio 1 : 2)

The appropriate dihydrazide (20 mmol) was added to a solution of Cp_2ZrCl_2 (10 mmol) in dry tetrahydrofuran (60 ml). To this n-butylamine (10 mmol) was added and the mixture stirred for 50–60 h. The precipitated complex was removed and thoroughly washed with tetrahydrofuran.

(C) Reaction of products obtained from reaction A with β-diketones

To a tetrahydrofuran solution of the product of reaction A (20 mmol) was added an appropriate β-diketone (20 mmol) and glacial acetic acid (5 ml). A clear solution (pH ~ 3) was obtained. The reaction mixture was refluxed in a fractionating column for 16–25 h. The small amount of water generated was collected azeotropically. The brown precipitate thus obtained was thoroughly washed with tetrahydrofuran and dried in vacuo.

(D) Reactions of products obtained from reaction B with β-diketones

The appropriate β-diketone (30 mmol) was added to a benzene solution (60 ml) of the product of reaction B (15 mmol). To this was added 5 ml of glacial acetic acid and the reaction mixture was refluxed for 20–32 h. The precipitated complex was removed by filtration and thoroughly washed with benzene.

Details of the reactions and the analytical data of the complexes are given in Table 1.

Results and discussion

A systematic study of the reactions of dicyclopentadienylzirconium(IV) dichloride (1 mol) with dihydrazides (oxalic, succinic, adipic) (1 mol or 2 mol) in the presence of base using tetrahydrofuran as solvent was carried out. The $[Cp_2Zr(L)]$ and $[CpZr(LH)_2Cl]$ complexes were obtained according to the following equations:

$$Cp_2ZrCl_2 + LH_2 + Et_3N \xrightarrow{THF} [Cp_2Zr(L)] + 2Et_3N \cdot HCl\downarrow \quad \textbf{(A)}$$

$$Cp_2ZrCl_2 + 2LH_2 + BuNH_2 \xrightarrow{THF} [CpZr(LH)_2Cl]\downarrow + BuNH_2 \cdot HCl + C_5H_6 \quad \textbf{(B)}$$

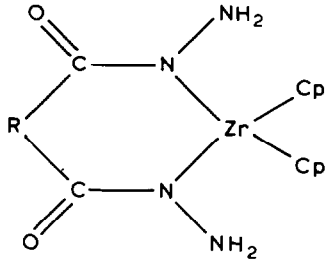
The elemental analyses (Table 1) are compatible with a 1:1 and 1:2 metal to ligand stoichiometry for complexes **A** and **B**, respectively. Type **A** complexes are soluble in tetrahydrofuran, chloroform, dimethylformamide, dimethylsulphoxide while type **B** complexes are soluble in benzene, toluene, dimethylformamide and dimethylsulphoxide. The electrical conductances of the complexes in DMF are consistent with non-electrolytes. The magnetic susceptibilities measured at room temperature by Gouy's method using $CuSO_4$ as calibrator showed all the complexes to be diamagnetic. The electronic spectra of all these complexes showed a single band in the region of 22500–23400 cm^{-1} which was assigned to the charge-transfer band and is in accordance with $(n-1)d^0ns^0$ electronic configuration.

The free dihydrazide ligands exhibit bands at ca. 1700–1680, 1545–1510, 2180–1260, 685–670 and 485–470 cm^{-1} in their infrared spectra attributable to amide-I (ν(C=O)), amide-II (ν(C–N) + δ(N–H)), amide-III (δ(N–H)) and amide-IV (δ(C=O)) and amide-VI (π(C=O)), respectively [16–18]. In complexes of type **A**, the amide-II and amide-III bands vanish. This may be taken as evidence of the coordination of the amide nitrogen to zirconium atom through deprotonation. The amide-I band is almost unperturbed suggesting the nonparticipation of the amide oxygen atoms (ketonic/enolic form) in coordinating to the metal. The ν(Zr–N) vibrations appear at ca. 450–435 cm^{-1}. However, complexes of type **B** show bands in the 1490–1480 and 1250–1230 cm^{-1} regions due to amide-II and amide-III vibrations, respectively. The negative shift in the position of these two bands indicates [19] the coordination of amide-nitrogen atoms to zirconium. The bands at ca. 450–440 cm^{-1} also appear in these complexes and are assignable to ν(Zr–N) [15]. Since complexes of type **B** are non-electrolytes and have a 1:2 metal to ligand stoichiometry, it appears that the ligands are coordinated to the metal through deprotonated and protonated nitrogen atoms. The ligand bands at ca. 3200 and 1650 cm^{-1} due to ν(NH) and $\delta(NH_2)$ vibrations, respectively, remain unchanged in the complexes indicating non-coordination of the terminal hydrazinic nitrogen atoms to the zirconium atom. In addition, all these complexes show bands at ~ 3000 ν(C–H), ~ 1430 ν(C–C) and ~ 1020, 800 in- and out-of-plane, respectively δ(C–H), characteristic of the cyclopentadienyl ring. The persistence of bands due to the cyclopentadienyl rings in the spectra of the complexes indicates that these

groups remain delocalized, are π-bonded (η^5) to the metal and retain their aromatic nature.

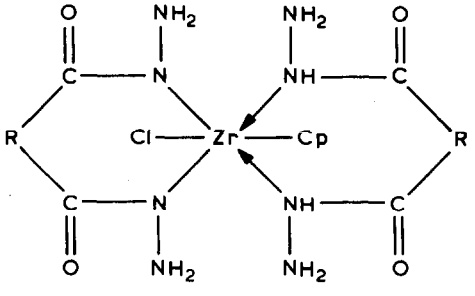
The proton magnetic resonance spectra of the free ligands in DMSO-d_6 show signals at ca. δ 4.85 and 4.30 ppm due to NH and NH_2 protons, respectively. In all the complexes, the signal due to the NH_2 group occurs at the same position. However, in complexes of type **A**, the signal due to the NH proton vanishes, and in complexes of type **B**, this undergoes downfield shift. The resonance line for the protons on the C_5H_5 ring always falls near δ 6.65–6.80 ppm. The appearance of a single, sharp signal for the protons of the cyclopentadienyl ring indicates rapid rotation of the ring about the metal-ring axis. The integrated proton ratios correspond to the proposed formulae.

Thus, on the basis of the discussion above, if the complexes **A** assume a monomeric form the following structure (**1**) may be proposed:

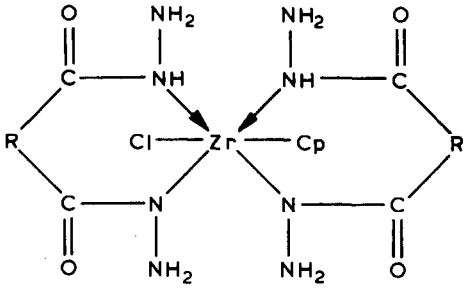


(1)

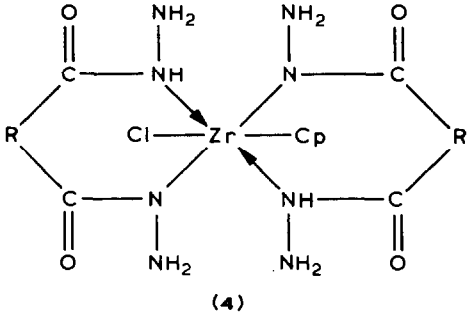
However, different structures (**2–4**) are possible for complexes of type **B** depending upon whether or not the two amide groups in the same ligand are deprotonated,



(2)



(3)

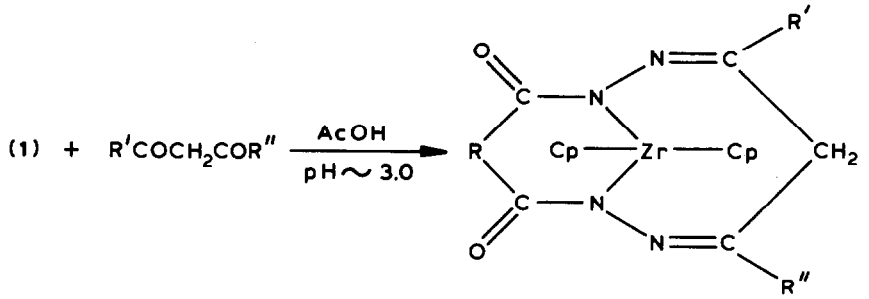


(4)

as opposed to one each from two different ligand molecules. The presence of secondary amide groups (–CONH–) is also indicated by a positive Liebermann's test [12].

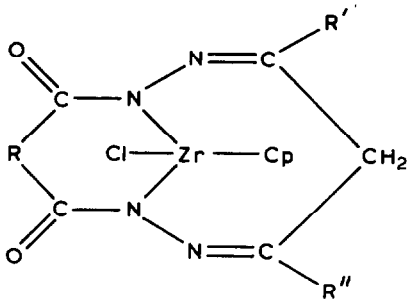
Reactions of dihydrazide complexes with β-diketones

The zirconium(IV) complexes of dihydrazides still possess two terminal hydrazinic nitrogen atoms each having a pair of unshared electrons. Accordingly, these groups can participate in nucleophilic condensation with β-diketones. The analytical



(5)

R′	R″
CH_3	CH_3
C_6H_5	CH_3
C_6H_5	C_6H_5
C_4H_3S	CF_3



(6)

data of these complexes are given in Table 1. These complexes were found to be soluble in dimethylformamide and dimethylsulphoxide. The electrical conductance measurements indicate their non-electrolytic nature. All these complexes are diamagnetic.

The infrared spectra of these cyclic products do not show any bands in the ν(NH) and $\delta(NH_2)$ regions. Instead, a new band appears at ca. 1620 cm^{-1} which is attributed to a C=N stretching mode of a newly formed azomethine linkage [16]. This indicates clearly that two terminal hydrazinic amino groups of the dihydrazide complexes condense with carbonyl oxygen atoms of the β-diketone giving rise to a cyclic molecule. These complexes do not respond to Liebermann's test indicating the

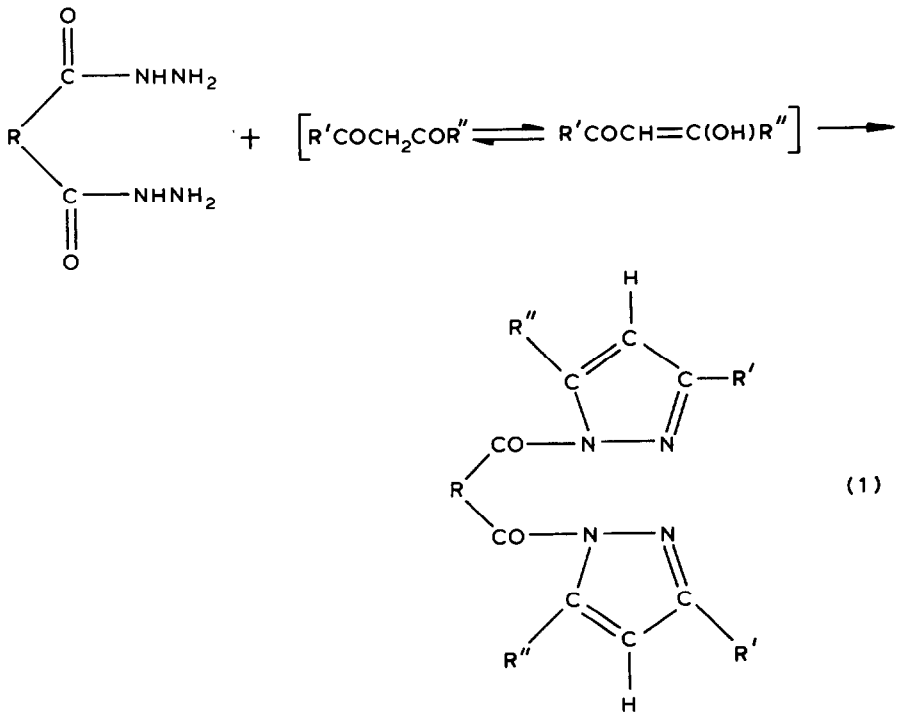
absence of secondary amide nitrogen. Other infrared spectral bands are similar to those observed for parent dihydrazide complexes.

The ^1H NMR spectra of these cyclic products do not show any peaks due to the NH or NH_2 protons. The signal due to the cyclopentadienyl protons appears at ca. δ6.60–6.80 ppm. The integrated proton ratios indicate the presence of two cyclopentadienyl rings in complexes **5** and only one in complexes **6**. The peak for CH_2 protons of the β-diketones appear at ca. δ3.60–3.80 ppm.

The formation of the products **6** from **2**, **3** or **4** can be explained on the assumption that the zirconium(IV) cation dissociates from the complex during the course of the reaction, and that subsequent reaction of the free ligand with the β-diketone in the presence of the metal ion (template effect) (Scheme 1) giving a cyclic complex.

It is likely that for steric reasons the complex **2**, **3** or **4** reacts with a β-diketone to form a highly strained cyclic compound which is immediately converted to a more stable compound having the structure **6**, as established from spectral studies.

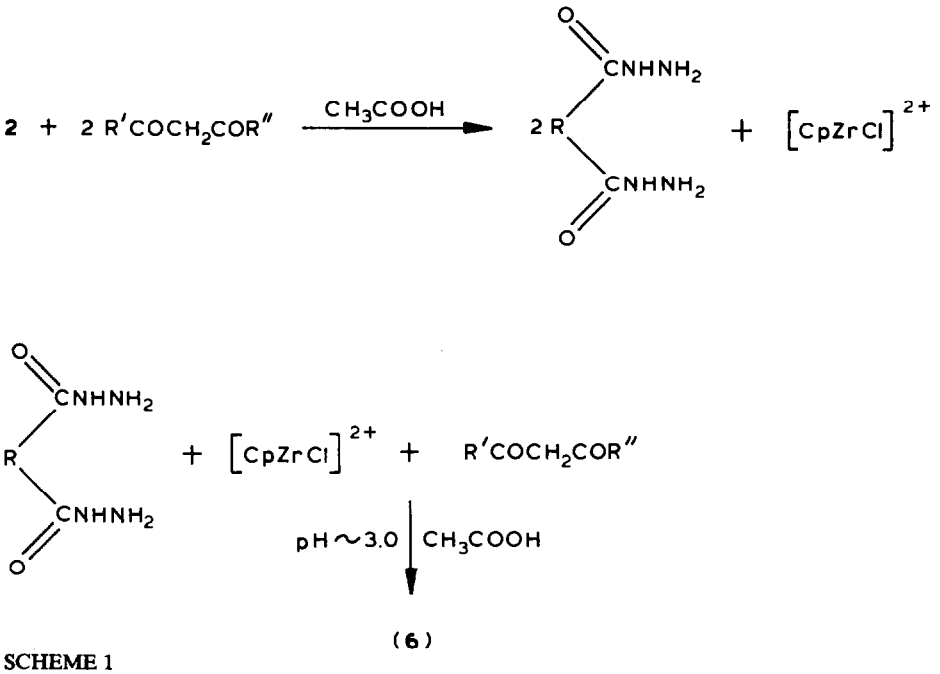
The zirconium(IV) cation in these reactions appears to function as a 'metal template' because in the absence of the metal ion a pyrazole ring is formed [21] by the reaction of hydrazine with β-diketone, see eq. 1. Thus, the formation of a



(1)

pyrazole derivative appears to be a function of the presence of a labile hydrogen atom at the β-nitrogen atom of the hydrazine. These labile protons are deprotonated in the presence of the dicyclopentadienylzirconium(IV) cation preventing the formation of the pyrazole ring giving instead a cyclic compound.

At present attempts are being made to displace the zirconium atom from the macrocyclic complexes in order to obtain the free pure macrocycle.



SCHEME 1

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