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SYNTHESES AND STRUCTURAL STUDIES ON PICOLINOYL, NICOTINOYL AND ISONICOTINOYL HYDRAZONE DERIVATIVES OF DICYCLOPENTADIENYLZIRCONIUM(IV)

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Summary

The reactions of dicyclopentadienylzirconium(IV) dichloride with picolinoyl, nicotinoyl and isonicotinoyl hydrazones derived from the appropriate acid hydrazides and acetone, acetophenone, salicylaldehyde or *o*-hydroxyacetophenone, have been studied in anhydrous tetrahydrofuran or dichloromethane in the presence or absence of amine using different molar ratios. Tentative structural conclusions are drawn for the reaction products based upon elemental analysis, electrical conductance, magnetic moment and spectral data (electronic, infrared and ^{1}H NMR). These ligands behave as neutral or deprotonated chelating agents. The coordination behaviour depends upon the pH of the medium, the nature of the substituent and the position of the hydrazone group relative to the pyridine nitrogen nucleus.

Introduction

The biochemical importance of heterocyclic acid amides and their derivatives is well documented [1–3]. The acid amide group itself is known to play a significant role in many biological processes. On the other hand, metal binding properties of acid amides are of special relevance to the chemistry of proteins which contain a number of amide linkages in their structure. Transition metal complexes of the amides of pyridine carboxylic acids have attracted a considerable amount of attention not only because of their potential biochemical applications but also because of the various bonding and stereochemical possibilities that they offer [4–11]. These ligands that contain an amide bond and are capable of undergoing keto $\rightleftharpoons$ enol tautomerism can coordinate to a metal atom through nitrogen or through oxygen or simultaneously through both nitrogen and oxygen.

A survey of literature revealed that no work has been done on the reactions of dicyclopentadienylzirconium(IV) dichloride with heterocyclic acid hydrazones. It was, therefore, considered of interest to carry out systematically reactions of Cp_2ZrCl_2 with various types of hydrazones.

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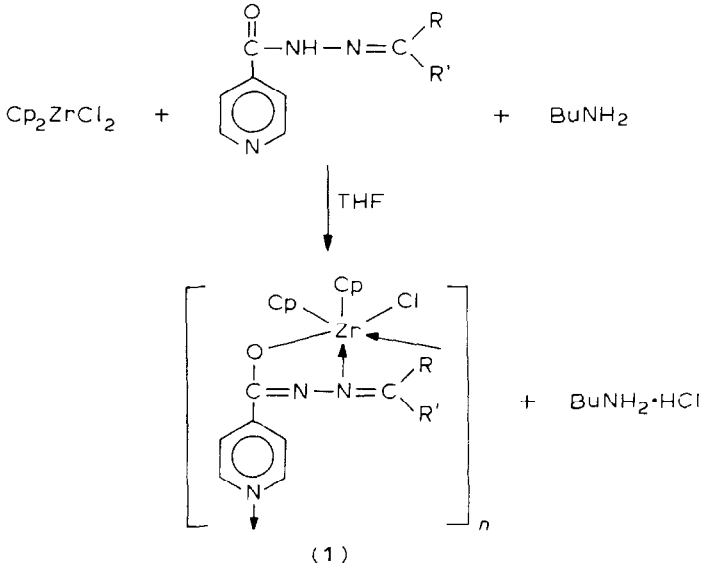
Results and discussion

(a) Isonicotinoyl hydrazone derivatives

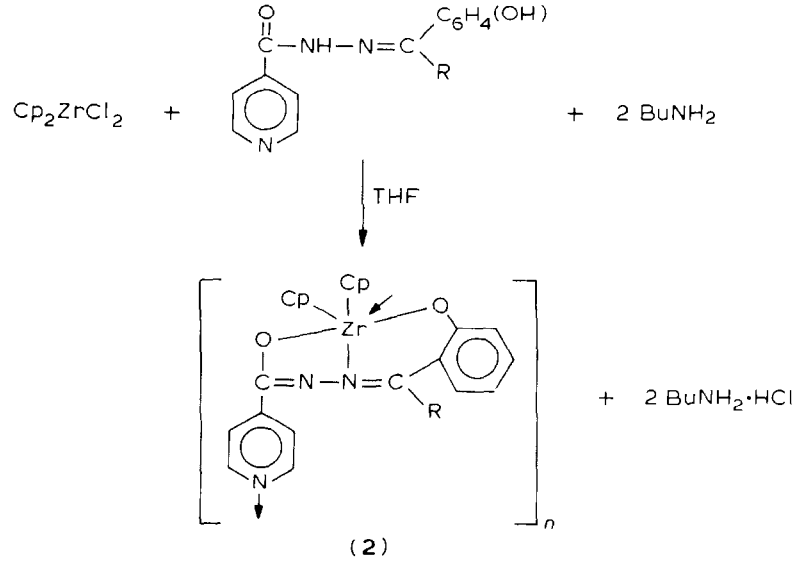
Dicyclopentadienylzirconium(IV) dichloride was allowed to react with acetone, acetophenone, salicylaldehyde and *o*-hydroxyacetophenone isonicotinoyl hy-



(1)

(R = CH_3, R' = CH_3 ; R = CH_3, R' = C_6H_5)

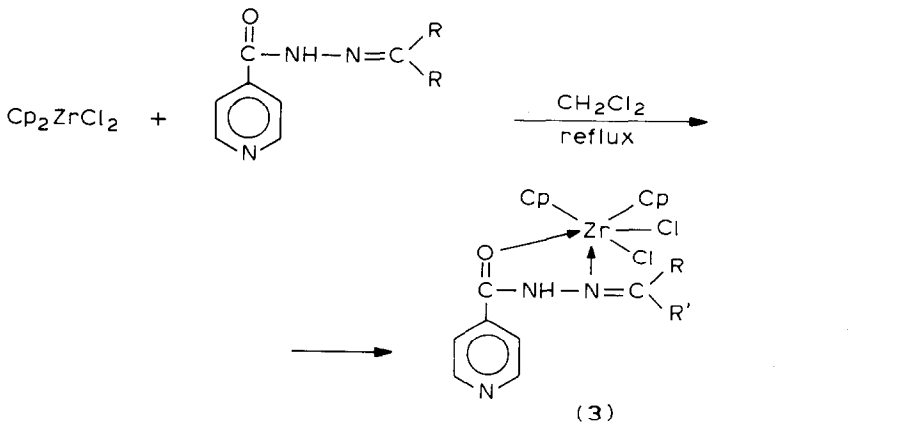
SCHEME 1. Reactions of dicyclopentadienylzirconium(IV) dichloride with acetone or acetophenone isonicotinoyl hydrazones.



(2)

(R = H or CH_3)

SCHEME 2. Reactions of dicyclopentadienylzirconium(IV) dichloride with salicylaldehyde or *o*-hydroxyacetophenone isonicotinoyl hydrazones.



(R = CH_3, R' = CH_3 ; R = CH_3, R' = C_6H_5)

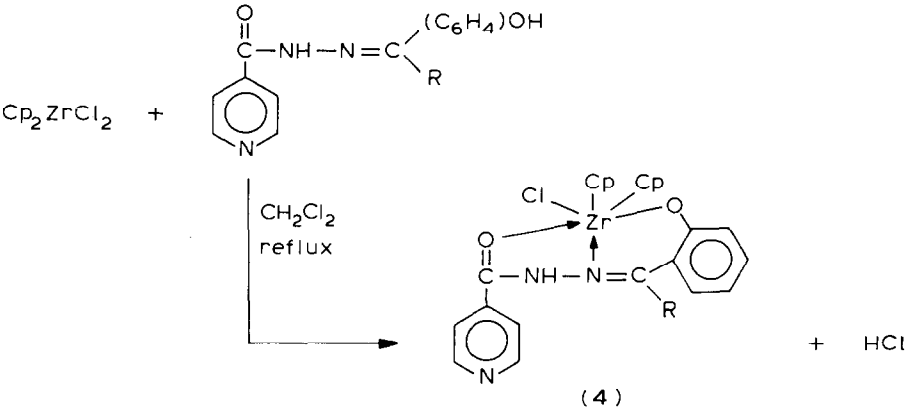
SCHEME 3. Reactions of dicyclopentadienylzirconium(IV) dichloride with acetone or acetophenone isonicotinoyl hydrazones in the absence of amine.

drazones in 1/1 molar ratio in tetrahydrofuran using butylamine as the proton acceptor. The reactions are given in Schemes 1 and 2.

A systematic study of the reactions of bis(cyclopentadienyl)zirconium(IV) dichloride with these ligands in the absence of amine has also been carried out in refluxing dichloromethane. The reactions are given in Schemes 3 and 4.

The reactions of dicyclopentadienylzirconium(IV) dichloride with isonicotinoyl hydrazones in 1/2 and 1/3 molar ratios, respectively, in the presence and absence of amine, have also been studied, but in all such cases only the 1/1 products have been isolated. The purity of these derivatives has been checked by TLC.

The analytical data in Table 1 show that isonicotinoyl hydrazones form two types of complexes, viz., the adducts and the deprotonated complexes. The ligands remain



(R = H or CH_3)

SCHEME 4. Reactions of dicyclopentadienylzirconium(IV) dichloride with salicylaldehyde or *o*-hydroxyacetophenone isonicotinoyl hydrazones in the absence of amine.

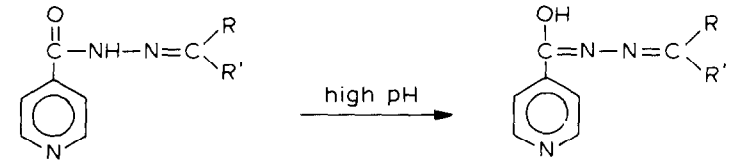
TABLE 1

REACTIONS OF Cp_2ZrCl_2 WITH ISONICOTINOYL HYDRAZONES

Reactants (molar ratio)	Solvent	Stirring or refluxing time (h)	Product	Yield (%)	Colour	Decomp. temp. (°C)	Analyses (Found (calcd.)(%))				
							C	H	N	Zr	Cl
Cp_2ZrCl_2 + AINH–H [a] + $BuNH_2$ (1/1/1)	THF	60	$[Cp_2Zr(AINH)Cl]_n$	65	Dark-yellow	230	52.5 (52.7)	4.5 (4.6)	9.5 (9.7)	21.0 (21.0)	8.2 (8.2)
Cp_2ZrCl_2 + AcINH–H [b] + $BuNH_2$ (1/1/1)	THF	60	$[Cp_2Zr(AcINH)Cl]_n$	62	Brown	225	58.0 (58.2)	4.3 (4.4)	8.4 (8.5)	18.4 (18.4)	7.1 (7.2)
Cp_2ZrCl_2 + SIN–H_2 [c] + $BuNH_2$ (1/1/2)	THF	50	$[Cp_2Zr(SINH)]_n$	60	Yellow	282	59.9 (60.0)	4.0 (4.1)	9.0 (9.1)	19.8 (19.8)	–
Cp_2ZrCl_2 + OINH–H_2 [d] + $BuNH_2$ (1/1/2)	THF	55	$[Cp_2Zr(OINH)]_n$	68	Dark-yellow	254	60.6 (60.7)	4.2 (4.4)	8.7 (8.8)	19.2 (19.2)	–
Cp_2ZrCl_2 + AINH–H (1/1)	CH_2Cl_2	40	$[Cp_2ZrCl_2(AINH–H)]$	55	Light-brown	186	48.6 (48.6)	4.4 (4.5)	8.4 (8.9)	19.3 (19.4)	15.1 (15.1)
Cp_2ZrCl_2 + AcINH–H (1/1)	CH_2Cl_2	40	$[Cp_2ZrCl_2(AcINH–H)]$	58	Yellow	167	54.2 (54.2)	4.3 (4.3)	7.8 (7.9)	17.0 (17.2)	13.4 (13.4)
Cp_2ZrCl_2 + SINH–H_2 (1/1)	CH_2Cl_2	20	$[Cp_2ZrCl(SINH–H)]$	70	Yellowish brown	172	55.5 (55.6)	4.0 (4.0)	8.2 (8.4)	18.4 (18.4)	7.0 (7.1)
Cp_2ZrCl_2 + OINH–H_2 (1/1)	CH_2Cl_2	25	$[Cp_2ZrCl(OINH–H)]$	59	Light-yellow	180	56.3 (56.4)	4.3 (4.3)	8.0 (8.2)	17.8 (17.8)	6.9 (6.9)

[a] AINH–H = Acetone isonicotinoyl hydrazone. [b] AcINH–H = Acetophenone isonicotinoyl hydrazone. [c] SINH–H_2 = Salicylaldehyde isonicotinoyl hydrazone. [d] OINH–H_2 = *o*-Hydroxyacetophenone isonicotinoyl hydrazone.

in the keto form **a** in acidic medium but are changed to the enolic form **b** on raising the pH. This permits the formation of addition compounds in keto form and deprotonated complexes at high pH by removal of the enolic proton.

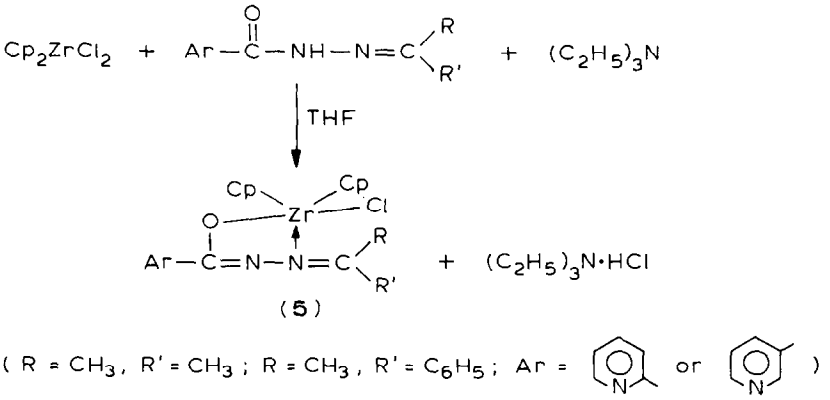


keto form (a) enolic form (b)

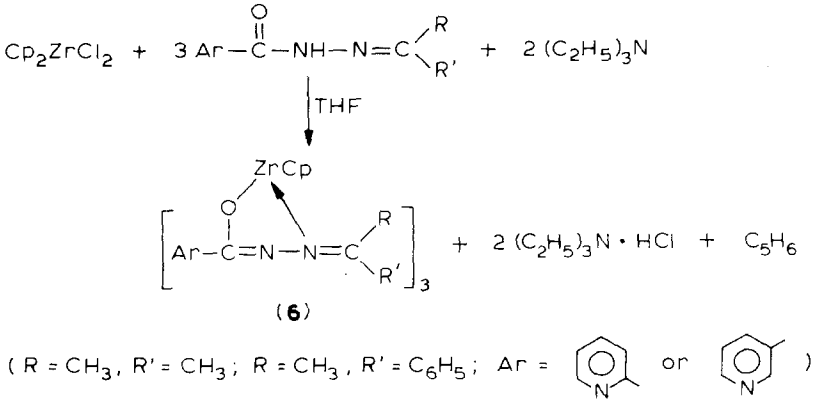
These complexes are yellow to brown in colour. The derivatives of types **1** and **2** are found to be insoluble in most of the common organic solvents except for dimethylformamide and dimethylsulfoxide. The derivatives of types **3** and **4** are soluble in tetrahydrofuran, methanol, benzene, dichloromethane, nitrobenzene and dimethylformamide. The electrical conductance measurements in dimethylformamide indicate their non-electrolytic nature. The magnetic susceptibility measurements indicate the diamagnetic nature of the complexes. The electronic spectra of all these complexes recorded in Nujol mulls show a single band in the 23,200–23,800 cm^{-1} region, assigned to a charge-transfer band. This is in accord with their $(n-1)d^0$, ns^0 electronic configuration.

(b) Picolinoyl and nicotinoyl hydrazone derivatives

Picolinoyl and nicotinoyl hydrazones, similar to isonicotinoyl hydrazone undergo keto–enol tautomerism and form two types of derivatives, viz., adduct and deprotonated complexes with dicyclopentadienylzirconium(IV) dichloride depending upon the pH of the medium. The coordination behaviours of picotinoyl and nicotinoyl hydrazones are found to be similar towards zirconium but differ from those of isonicotinoyl hydrozones. In those derivatives, the pyridine nitrogen does not participate in coordination. On the other hand, in the presence of amine, acetone and acetophenone picolinoyl/nicotinoyl hydrazones also react with dicyclopenta-



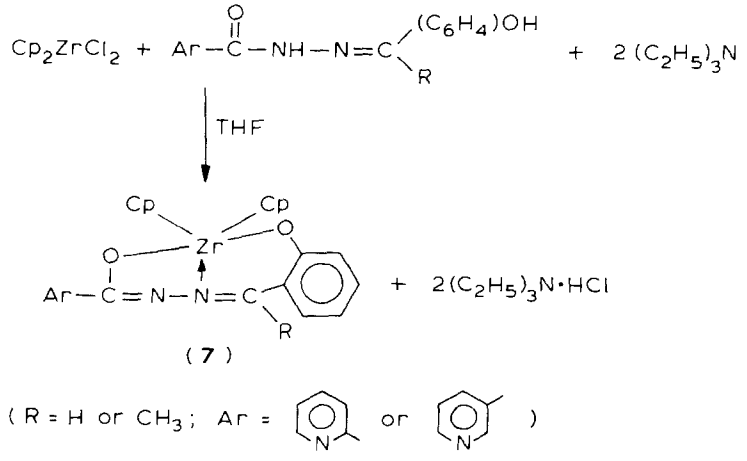
SCHEME 5. Reactions of dicyclopentadienylzirconium(IV) dichloride with acetone or acetophenone picolinoyl/nicotinoyl hydrazones (molar ratio 1/1).



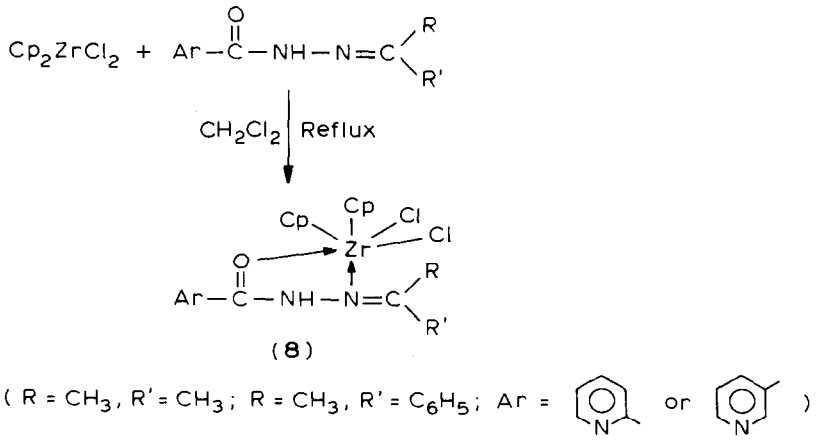
SCHEME 6. Reactions of dicyclopentadienylzirconium(IV) dichloride with acetone or acetophenone picolinoyl/nicotinoyl hydrazones (molar ratio 1/3).

dienylzirconium(IV) dichloride in a 3/1 molar ratio, respectively, forming monocyclopentadienyl-tris(hydrazone) derivatives. The reactions of the above ligands with metal salts in 2/1 molar ratios, respectively, give a mixture of 1/1 and 3/1 derivatives. The two types of compounds present in the mixture were separated by TLC. The following types of derivatives have been isolated.

The analytical and physical data of picolinoyl and nicotinoyl hydrazone derivatives are given in Tables 2 and 3, respectively. The methods used for the preparation and isolation of these compounds give materials of good purity, as confirmed by their analyses and TLC. All these complexes are coloured. They are quite stable in air, but their solutions are hydrolyzed on standing. Conductance measurements reveal that they are essentially non-electrolytes. Magnetic susceptibility values at room temperature show the diamagnetic nature of the complexes. The electronic



SCHEME 7. Reactions of dicyclopentadienylzirconium(IV) dichloride with salicylaldehyde or *o*-hydroxyacetophenone picolinoyl/nicotinoyl hydrazones.



SCHEME 8. Reactions of dicyclopentadienylzirconium(IV) dichloride with acetone or acetophenone picolinoyl/nicotinoyl hydrazones in the absence of amine.

spectra of all these complexes show a single band in the region 22,500–23,200 cm^{-1} which can be assigned to the charge-transfer band.

Infrared spectra

The bonding sites of hydrazones involved in the adducts as well as the deprotonated complexes have been determined by careful comparison of the infrared spectra of the complexes with the spectra of ligands.

Amino and amide group vibrations. The ν(NH) band appears at about 3200 cm^{-1} in the ligands. The position of this band remains unaffected in the spectra of the adducts of types **3**, **4**, **8** and **9** but it disappears in the spectra of deprotonated complexes **1**, **2**, **5**, **6** and **7**. All those ligands show bands in the region 1660–1675, 1550–1560 and 1300 cm^{-1}, assignable [12] to amide-I (ν(C=O)), amide-II (ν(CN) +

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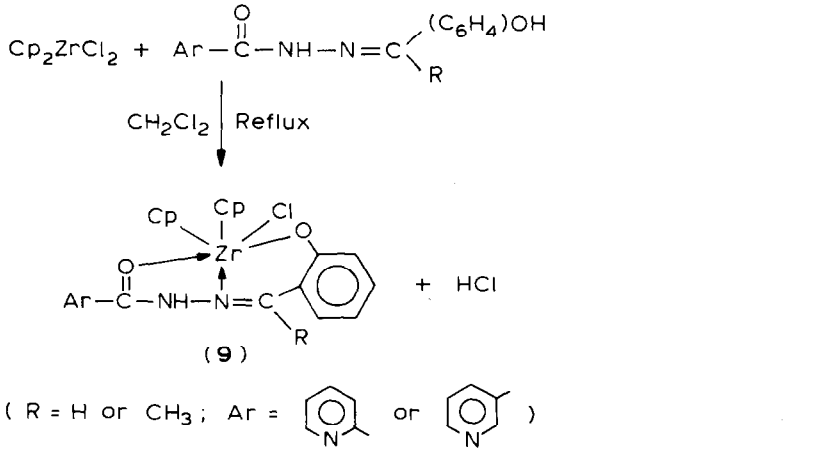

SCHEME 9. Reactions of dicyclopentadienylzirconium(IV) dichloride with salicylaldehyde or *o*-hydroxyacetophenone picolinoyl/nicotinoyl hydrazones in the absence of amine.

TABLE 2

REACTIONS OF Cp_2ZrCl_2 WITH PICOLINOYL HYDRAZONES

Reactants (molar ratio)	Solvent	Stirring or refluxing time (h)	Product	Yield (%)	Colour	Decom. temp. (°C)	Analyses (Found (calcd.)(%))				
							C	H	N	Zr	Cl
Cp_2ZrCl_2 + APH–H [a] + Et_3N (1/1/1)	THF	30	[Cp_2Zr(APH)Cl]	58	Yellow	186	52.7 (52.7)	4.4 (4.6)	9.7 (9.7)	21.0 (21.0)	8.1 (8.2)
Cp_2ZrCl_2 + AcPH [b]–H + Et_3N (1/1/1)	THF	40	[Cp_2Zr(AcPH)Cl]	60	Yellow	132	58.2 (58.2)	4.2 (4.5)	8.3 (8.5)	18.2 (18.4)	7.2 (7.2)
Cp_2ZrCl_2 + APH–H + Et_3N (1/3/2)	THF	60	[$CpZr(APH)_3$]	55	Yellow	240	56.1 (56.1)	5.0 (5.1)	18.2 (18.4)	13.3 (13.3)	–
Cp_2ZrCl_2 + AcPH–H + Et_3N (1/3/2)	THF	70	[$CpZr(AcPH)_3$]	52	Light brown	265	64.7 (64.8)	4.5 (4.7)	14.4 (14.5)	10.5 (10.5)	–
Cp_2ZrCl_2 + SPH–H_2 [c] + Et_3N (1/1/12)	THF	30	[Cp_2Zr(SPH)]	65	Yellow	222	59.9 (60.0)	4.0 (4.1)	9.0 (9.1)	19.7 (19.8)	–
Cp_2ZrCl_2 + OPH–H_2 [d] + Et_3N (1/1/2)	THF	30	[Cp_2Zr(OPH)]	68	Light yellow	203	60.7 (60.7)	4.3 (4.4)	8.6 (8.8)	19.2 (19.2)	–
Cp_2ZrCl_2 + APH–H (1/1)	CH_2Cl_2	50	[Cp_2ZrCl_2(APH–H)]	52	Light brown	180	48.6 (48.6)	4.5 (4.5)	8.7 (8.9)	19.2 (19.4)	15.1 (15.1)
Cp_2ZrCl_2 + AcPH–H (1/1)	CH_2Cl_2	50	[Cp_2ZrCl_2(AcPH–H)]	54	Brown	160	54.2 (54.2)	4.2 (4.3)	7.7 (7.9)	17.2 (17.2)	13.3 (13.4)
Cp_2ZrCl_2 + SPH–H_2 (1/1)	CH_2Cl_2	25	[Cp_2Zr(SPH–H)Cl]	60	Yellowish brown	192	55.6 (55.6)	3.8 (4.0)	8.4 (8.4)	18.3 (18.4)	7.1 (7.1)
Cp_2ZrCl_2 + OPH–H_2 (1/1)	CH_2Cl_2	30	[Cp_2Zr(OPH–H)Cl]	63	Yellowish brown	187	56.4 (56.4)	4.3 (4.3)	8.0 (8.2)	17.7 (17.8)	6.8 (6.9)

[a] APH–H = Acetone picotinoyl hydrazone. [b] AcPH–H = Acetophenone picotinoyl hydrazone. [c] SPH–H_2 = Salicylaldehydepicotinoyl hydrazone. [d] OPH–H_2 = *o*-Hydroxyacetophenone picotinoyl hydrazone.

TABLE 3

REACTIONS OF Cp_2ZrCl_2 WITH NICOTINOYL HYDRAZONE

Reactants (molar ratio)	Solvent	Stirring or refluxing time (h)	Product	Yield (%)	Colour	Decomp. temp. (°C)	Analyses (Found (calcd.)(%))				
							C	H	N	Zr	Cl
Cp_2ZrCl_2 + ANH–H [a] + Et_3N (1/1/1)	THF	40	[Cp_2Zr(ANH)Cl]	65	Brown	179	52.7 (52.7)	4.4 (4.6)	9.5 (9.7)	21.0 (21.0	8.2 (8.2)
Cp_2ZrCl_2 + AcNH–H [b] + Et_3N (1/1/1)	THF	40	[Cp_2Zr(AcNH)Cl]	68	Brown	204	58.2 (58.2)	4.4 (4.4)	8.3 (8.5)	18.4 (18.4)	7.1 (7.2)
Cp_2ZrCl_2 + NH–H + Et_3N (1/3/2)	THF	60	[$CpZr(ANH)_3$]	55	Light-brown	294	56.1 (56.1)	5.0 (5.1)	18.2 (18.4)	13.2 (13.3)	–
Cp_2ZrCl_2 + AcNH–H + Et_3N (1/3/2)	THF	60	[$CpZr(AcNH)_3$]	59	Light-brown	232	64.8 (63.8)	4.6 (4.7)	14.5 (14.5)	10.4 (10.5)	–
Cp_2ZrCl_2 + SNH–H_2 [c] + Et_3N (1/1/2)	THF	30	[Cp_2Zr(SNH)]	64	Yellow	252	59.9 (60.0)	4.0 (4.1)	8.9 (9.1)	19.8 (19.8)	–
Cp_2ZrCl_2 + OHN–H_2 [d] + Et_3N (1/1/2)	THF	30	[Cp_2Zr(ONH)]	68	Yellow	208	60.7 (60.7)	4.4 (4.4)	8.6 (8.8)	19.2 (19.2)	–
Cp_2ZrCl_2 + ANH–H (1/1)	CH_2Cl_2	40	[Cp_2ZrCl_2(ANH–H)]	60	Cream	152	48.5 (48.6)	4.5 4.5)	8.6 (8.9)	19.4 (19.4)	15.0 (15.1)
Cp_2ZrCl_2 + AcNH–H (1/1)	CH_2Cl_2	40	[Cp_2ZrCl_2(AcNH–H)]	62	Light-yellow	181	54.0 (54.2)	4.3 (4.3)	7.8 (7.9)	17.1 (17.2)	13.4 (13.4)
Cp_2ZrCl_2 + SNH–H_2 (1/1)	CH_2Cl_2	20	[Cp_2Zr(SNH–H)Cl]	70	Light-yellow	179	55.5 (55.6)	4.0 (4.0)	8.2 (8.4)	18.4 (18.4)	6.9 (7.1)
Cp_2ZrCl_2 + ONH–H_2 (1/1)	CH_2Cl_2	30	[Cp_2Zr(ONH–H)Cl]	68	Yellow	162	56.4 (56.4)	4.2 (4.3)	8.1 (8.2)	17.8 (17.8)	6.9 (6.9)

[a] ANH–H = Acetone nicotinoyl hydrazone. [b] AcNH–H = Acetophenone nicotinoyl hydrazone. [c] SNH–H_2 = Salicylaldehyde nicotinoyl hydrazone. [d] ONH–H_2 = *o*-Hydroxyacetophenone nicotinoyl hydrazone.

δ(NH)) and amide-III (δ(NH)) vibrations, respectively. Negative shifts of amide-I ($\sim$ 15–20 cm^{-1}) and amide-II ($\sim$ 20 cm^{-1}) bands and a positive shift of amide-III band ($>$ 25–30 cm^{-1}) in the spectra of the adducts of types **3**, **4**, **8** and **9** indicate [12] coordination through the carbonyl oxygen. These bands disappear in the deprotonated complexes of types **1**, **2**, **5**, **6** and **7** suggesting [9] enolization of the keto group by the formation of complexes through deprotonation. The presence of strong characteristic bands ν(C=N) and $\nu(NCO^-)$ in 1585–1600 and 1530–1540 cm^{-1} regions, respectively, further support the enolization of the keto group.

Azomethine group vibration. All these ligands show a weak band at ca. 1625–1630 cm^{-1}, which can be assigned to ν(C=N) vibration of the azomethine linkage. The appearance of a weak ν(C=N) band is in accord with the observations of several other workers [13,14]. The band due to ν(C=N) appears at a slightly lower wavenumber ($\sim$ 1610 cm^{-1}) in all the complexes suggesting [12] that the nitrogen atom of the azomethine group is coordinated to a zirconium atom. The ligand ν(N–N) band at about 1020–1035 cm^{-1} is shifted considerably ($\sim$ 20–25 cm^{-1}) to higher wavenumber in all the complexes, further suggesting the coordination through the azomethine nitrogen.

Phenolic group vibration. The picolinoyl, nicotinoyl and isonicotinoyl hydrazones derived from salicylaldehyde and *o*-hydroxyacetophenone show bands due to ν(OH) at about 3400 cm^{-1}. In their complexes, this band disappears indicating the deprotonation of the phenolic group.

Pyridine ring vibrations. The pyridine ring vibrations most affected by pyridine nitrogen coordination to the metal atom are 8a (pyridine ring deformation), 6a (in-plane ring deformation) and 16b (out-of-plane deformation) [15–16]. These vibrations appear at ca. 1560, 620 and 410 cm^{-1}, respectively, in the free ligands. In all the complexes, except in the adducts formed by isonicotinoyl hydrazones of types **1** and **2**, the position of these bands remain unaffected indicating the non-participation of pyridine nitrogen in coordination. However, only in two types of derivatives **1** and **2**, all these bands show upward shifts ($\sim$ 10–20 cm^{-1}) indicating [12] pyridine nitrogen coordination. In these deprotonated complexes, the simultaneous bonding of the enolic oxygen, azomethine and ring nitrogen with the same zirconium atom is ruled out for steric reasons and consequently, the ring nitrogen must coordinate with another zirconium atom yielding polymeric structures.

Metal–ligand vibrations. The non-ligand bands in the spectra of the complexes in the 500–510, 460–480, 430–445, 350 and 270–260 cm^{-1} regions are assigned [17] to ν(Zr–O(Phenolic), ν(Zr–N), ν(Zr–O) (Ketonic), ν(Zr–Cl) and ν(Zr–py) modes, respectively.

Cyclopentadienyl ring vibrations. In addition to the above bands, the absorption bands occurring at ca. 3000 cm^{-1} (C–H stretch), ca. 1435 cm^{-1} (C–C stretch) and ca. 810 cm^{-1} (CH out-of-plane deformation) in all the complexes indicate the presence of cyclopentadienyl rings. All these bands correspond [18] to those of dicyclopentadienylzirconium(IV) dichloride.

^{1}H NMR spectra

The ^{1}H NMR spectra of these complexes were recorded in deuterated chloroform and dimethylformamide. The intensities of all the resonance lines were determined by planimetric integration. The following conclusions can be derived by comparing the spectra of the ligands and their corresponding complexes.

(i) A signal in all the derivatives at δ6.5–6.8 ppm may be assigned to the protons of the cyclopentadienyl ring. The appearance of a single sharp cyclopentadienyl resonance is attributed to the rapid rotation of the ring about the metal–ring axis.
(ii) The NMR spectra of these hydrazones display a signal at about δ11.3 ppm assignable to an NH proton. This signal disappears in the complexes **1**,**2**,**5**,**6** and **7**. This indicates that this proton is removed in deprotonated complexes.
(iii) The phenolic proton signal of salicylaldehyde and *o*-hydroxyacetophenone hydrazones at about δ12.4 ppm disappears in all of their complexes.
(iv) The signal due to pyridine protons in the spectra of different hydrazones appears at about δ8.9–8.0 ppm. This signal shifts downfield in complexes of types **1** and **2** and appears at about δ9.0–8.6 ppm indicating the involvement of ring nitrogen in bonding with zirconium(IV). However, in all other complexes, the position of this signal remains almost the same.
(v) The two kinetic possibilities, viz., whether metal-centred rearrangement is slow or fast, can be distinguished by analysis of the NMR spectra. In the tris(hydrazone) derivatives of types **6**, two distinct resonance lines for the protons of the ligands are observed which must result from the non-equivalent environments for the different ligands. The integrated proton ratios correspond to the proposed formulae.

Experimental

All the reactions were carried out under strictly anhydrous conditions. Tetrahydrofuran was dried on sodium wire and refluxed. Dichloromethane was dried over calcium hydride. Dicyclopentadienylzirconium(IV) dichloride was prepared by treatment of sodium cyclopentadienide and zirconium(IV) chloride in a nitrogen atmosphere [19]. The ligands were prepared as mentioned in the literature [20,21].

The analyses and physical measurement details were the same as those described earlier [17]. Zirconium was estimated gravimetrically as its oxide, after decomposing the complexes with nitric acid.

Reactions of dicyclopentadienylzirconium(IV) dichloride with isonicotinoyl hydrazones in the presence of amine

The appropriate hydrazone (30 mmol) was added to a solution of Cp_2ZrCl_2 (30 mmol) in dry tetrahydrofuran (60 ml). The n-butyl amine (30 mmol in the case of acetone and acetophenone isonicotinoyl hydrazones and 60 mmol in the case of salicylaldehyde and *o*-hydroxyacetophenone isonicotinoyl hydrazone) was added to this and the mixture was stirred for 50–60 h. The precipitated complex was removed, thoroughly washed with tetrahydrofuran and dried in vacuo.

Reactions of dicyclopentadienylzirconium(IV) dichloride with picolinoyl/nicotinoyl hydrazones (molar ratio 1/1) in the presence of amine

A mixture of Cp_2ZrCl_2 (30 mmol) and the appropriate hydrazone (30 mmol) was dissolved in dry tetrahydrofuran (60 ml) and dry triethylamine (30 mmol in the case of acetone and acetophenone hydrazones and 60 mmol in the cases of salicylaldehyde and *o*-hydroxyacetophenone hydrazones) was added. The contents were stirred for 30–40 h at room temperature. Precipitated triethylamine hydrochloride was removed by filtration and the clear filtrate was evaporated to dryness under reduced pressure. The complex was recrystallised from a THF/petroleum ether mixture.

Reactions of dicyclopentadienylzirconium(IV) dichloride with acetone and acetophenone picolinoyl / nicotinoyl hydrazones (molar ratio 1 / 3) in the presence of amine

Dry triethylamine (20 mmol) was added to dicyclopentadienylzirconium(IV) dichloride (10 mmol) and the appropriate hydrazone (30 mmol) in tetrahydrofuran (60 ml) and the mixture was stirred for 60–70 h at room temperature on a magnetic stirrer. Precipitated triethylamine hydrochloride was removed by fitration and the solvent was distilled off under reduced pressure. The product so obtained was crystallised from n-hexane/tetrahydrofuran.

Reactions of dicyclopentadienylzirconium(IV) dichloride with picolinoyl, nicotinoyl and isonicotinoyl hydrazones in the absence of amine

All these complexes were prepared by treating dicyclopentadienylzirconium(IV) dichloride with the corresponding ligand in equimolar ratios and adding about 60 ml of dry dichloromethane then refluxed for 20–50 h. The solutions were filtered and their volume reduced to about 20 ml. Further, addition of dry petroleum ether (60–80°C, 20 ml) to the above solutions and allowing them to stand overnight gave coloured crystals which were filtered and oven dried at 80°C.

Further details of the reactions, experimental and analytical data see Tables 1, 2 and 3.

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References

1 R.C. Elderfield, Heterocyclic compounds, John Wiley and Sons, New York, 1959.
2 N. Saha and D. Bhattacharyya, J. Ind. Chem. Soc., LIV (1977) 143.
3 J.R. Dilworth, Coord. Chem. Rev., 21 (1976) 29.
4 R.C. Aggarwal and B. Singh, Trans. Met. Chem., 1, 161 (1976) 275.
5 A. Dutta Ahmed and N. Roy Chaudhury, J. Inorg. Nucl. Chem., 31 (1969) 2545 and references therein.
6 D.K. Rastogi, S.K. Dua, V.B. Rana and S.K. Sahni, J. Coord. Chem., 8 (1978) 97; J. Inorg. Nucl. Chem., 40 (1978) 1323; Trans. Met. Chem., 3 (1978) 56.
7 R.C. Aggarwal and B. Singh, J. Coord. Chem., 7 (1978) 245; J. Inorg. Nucl. Chem., 40 (1978) 1174.
8 M. Nonoyama, S. Tomita and V. Yamasaki, Inorg. Chim. Acta, 12 (1975) 33.
9 R.C. Aggarwal and D.S.S. Rao, Ind. J. Chem., 21A (1982) 735; J. Inorg. Nucl. Chem., 43 (1981) 1922.
10 M.P. Teotia, J.N. Gurtu and V.B. Rana, Ind. J. Chem., 20A (1981) 520.
11 R.C. Aggarwal, T. Prasad and B.N. Yadav, J. Inorg. Nucl. Chem., 37 (1975) 899.
12 S.K. Sengupta, S.K. Sahni and R.N. Kapoor, J. Coord. Chem., 12 (1982) 113.
13 S. Kher, S.K. Sahni, V. Kumari and R.N. Kapoor, Inorg. Chim. Acta, 37 (1979) 121.
14 S.K. Sahni, Trans. Met. Chem., 4 (1979) 73.
15 D.P. Madden, M.M. daMota and S.M. Nelson, J. Chem. Soc., A (1970) 890.
16 D.P. Madden and S.M. Nelson, J. Chem. Soc., A (1970) 890.
17 V. Srivastava, O.P. Pandey, S.K. Sengupta and S.C. Tripathi, J. Organomet. Chem., 279 (1985) 395.
18 H.P. Fritz, Adv. Organomet. Chem., 1 (1967) 262.
19 G. Wilkinson and J.M. Birmingham, J. Am. Chem. Soc., 76 (1964) 4281.
20 H.H. Fox and J.T. Gibas, J. Org. Chem., 18 (1953) 983.
21 L.J. Sacconi, J. Am. Chem. Soc., 75 (1953) 5434.