

Synthesis and Characterization of Hydrazone and Azine Derivatives of Bis(cyclopentadienyl)titanium(IV)

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Synopsis. Pentacoordinated hydrazone and azine derivatives of bis(cyclopentadienyl)titanium(IV) of the type $[(OC_6H_4CR:NNHR')TiCl(Cp)_2]$ and $[(OC_6H_4CR'':NN:CR''C_6H_4O)Ti(Cp)_2]$, where $R=H$ or CH_3 , $R'=H$, C_6H_5 or $C_6H_3(NO_2)_2$ and $R''=H$ or CH_3 , have been prepared. The products were characterized by chemical analyses, electrical conductance, IR, 1H NMR, and electronic spectral studies.

Some hydrazone complexes and a few azine complexes of titanium have been studied.^{1–4} However, no systematic study on their organometallic derivatives is available. In view of the versatile chelating ability, widespread applications and lack of data involving organometallic derivatives of titanium, it has been considered of interest to study the reactions of Cp_2TiCl_2 with the title ligands.

Experimental

Physical Measurements. Conductance measurements were made in DMSO on a Systronic Digital Direct Reading Conductivity Meter Type 304. Solid state IR spectra were recorded in KBr pellets in the 4000–200 cm^{-1} region on a Perkin-Elmer 621 grating spectrophotometer. 1H NMR spectra were recorded in deuterated chloroform on a JEOL JNM-FX 200 Fourier Transform NMR spectrometer. Chemical shifts are expressed relative to an internal reference of TMS (1% by volume). The electronic spectra of these complexes were run on a Perkin-Elmer 4000 Å instrument.

Preparation of the Ligands. Hydrazones of salicylaldehyde and 2'-hydroxyacetophenone were prepared by the gradual addition of salicylaldehyde/2'-hydroxyacetophenone to the ethanolic solution of hydrazine hydrate, phenylhydrazine or 2,4-dinitrophenylhydrazine in equimolar ratio. Due to insoluble nature of 2,4-dinitrophenylhydrazine in ethanol, a minimum quantity of sulfuric acid was added into its ethanolic suspension to make its homogeneous solution. The mixture was stirred under reflux for half an hour and then cooled in an ice bath. The precipitate so obtained was filtered, washed with ethanol and recrystallized from hot ethanol or glacial acetic acid in case of 2,4-dinitrophenylhydrazone derivatives.

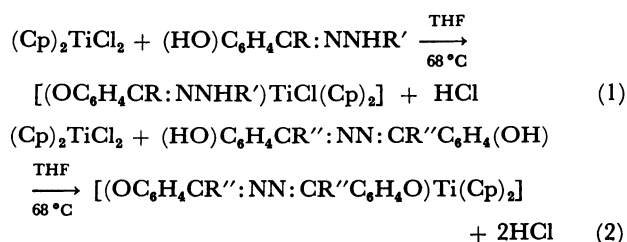
Azines were synthesized by the condensation reaction of salicylaldehyde or 2'-hydroxyacetophenone with hydrazine hydrate in 2:1 molar ratio in ethanol and the products were isolated in a similar manner as described for the hydrazones.

Preparation of Complexes. To a stirred solution of bis(cyclopentadienyl)titanium(IV)dichloride, $(Cp)_2TiCl_2$ (8 mmole) in 30 ml tetrahydrofuran, a solution containing 8 mmole of appropriate hydrazone or azine in 30 ml tetrahydrofuran was added slowly and the reaction mixture was refluxed for 10–12 h. It was then filtered and the volume of the filtrate was reduced to ca. 20 ml by evaporating the solvent under reduced pressure. The crystals of the product were precipitated by adding 80 ml petroleum ether (60–80 °C) to the concentrated filtrate. These were filtered, washed

with petroleum ether and dried under vacuum. Recrystallized from dichloromethane by adding excess of petroleum ether.

Results and Discussion

The reactions involved in the preparation of hydrazone and azine derivatives of bis(cyclopentadienyl)titanium(IV) may be represented according to equations 1 and 2, respectively as shown below:



where $R=H$ or CH_3 , $R'=H$, C_6H_5 or $C_6H_3(NO_2)_2$ and $R''=H$ or CH_3 .

Table 1 lists the analytical data and physical characteristics of the complexes. The satisfactory elemental analyses support the stoichiometry assigned to these complexes. These are moderately soluble in chloroform, dichloromethane, acetone, THF and DMSO. Electrical conductance measurements in DMSO show these complexes to be non-electrolytes.

Infrared Spectra. Absorption bands indicating the presence of cyclopentadienyl groups are found at ca. 3100 cm^{-1} $\nu(C-H)$, 1450 cm^{-1} $\nu(C-C)$, 1025 cm^{-1} $\nu(C-H)$ in plane and 810 cm^{-1} $\nu(C-C)$ out of plane.⁵ Apart from this, the band at 445 cm^{-1} may be assigned to $\nu(Ti-C_5H_5)$ vibrations.⁶

A strong band (due to the azomethine, $>C=N$ -group)^{7,8} at ca. 1630 cm^{-1} in the spectra of free hydrazone ligands is shifted to lower wave numbers (ca. 1600 cm^{-1}) in the complexes studied, showing the coordination of azomethine nitrogen to the metal.^{9,10} The N–N frequency found at ≈ 940 cm^{-1} in the free ligands is shifted to higher value (≈ 970 cm^{-1}).

A high intensity band at ca. 1265 cm^{-1} in the free hydrazone ligands may be assigned to the phenolic C–O stretching.^{7,8} In the complexes this band appears at ≈ 1290 cm^{-1} , indicating bonding of the hydrazone ligand through oxygen. Furthermore, $\nu(OH)$ band in the 3450–3390 cm^{-1} region disappears in the hydrazone complexes.

The coordination of methine nitrogen and bonding of the phenolic oxygen to the metal is supported by the appearance of two new absorption bands in the spectra of hydrazone derivatives at ca. 530–550 cm^{-1} and 430–470 cm^{-1} , which may be assigned to $\nu(Ti \leftarrow N)$ and $\nu(Ti-O)$ vibrations,² respectively. Band at ca. 380 cm^{-1} is the characteristic of $\nu(Ti-Cl)$ vibration.¹¹

TABLE 1. ANALYTICAL DATA AND PHYSICAL CHARACTERISTICS OF $[(OC_6H_4CR:NNHR')TiCl(Cp)_2]$ AND $[(OC_6H_4CR'':NN:CR''C_6H_4O)Ti(Cp)_2]$

R, R' or R''	Yield/%	Colour	Decomp temp °C	Found (Calcd) %				
				C	H	Ti	N	Cl
R=H, R'=H	62	Yellow	146—148	58.32 (58.55)	4.72 (4.88)	13.38 (13.75)	7.96 (8.04)	10.08 (10.19)
R=H, R'=C ₆ H ₅	60	Yellowish brown	152—155	65.19 (65.03)	4.74 (4.95)	11.07 (11.29)	6.51 (6.60)	8.13 (8.36)
R=H, R'=C ₆ H ₃ (NO ₂) ₂	78	Red	144—145	53.82 (53.65)	3.84 (3.69)	9.04 (9.31)	10.95 (10.89)	6.73 (6.90)
R=CH ₃ , R'=H	70	Pinkish red	186—187	59.46 (59.60)	5.00 (5.24)	13.09 (13.22)	7.59 (7.73)	9.64 (9.79)
R=CH ₃ , R'=C ₆ H ₅	68	Yellowish brown	178—181	65.48 (65.69)	5.42 (5.25)	10.62 (10.93)	6.32 (6.39)	8.16 (8.10)
R=CH ₃ , R'=C ₆ H ₃ (NO ₂) ₂	73	Orange	168—170	54.74 (54.50)	4.13 (3.97)	8.61 (9.06)	10.46 (10.60)	6.81 (6.72)
R''=H	68	Light brown	156—157	69.12 (69.25)	4.67 (4.81)	11.20 (11.52)	6.70 (6.73)	—
R''=CH ₃	65	Yellowish brown	142—143	70.07 (70.29)	5.30 (5.41)	10.67 (10.79)	6.16 (6.31)	—

As expected, the spectra of the azine complexes do not show $\nu(OH)$, $\nu(NH)$, and $\nu(Ti-Cl)$ vibrations. The splitting and lowering of the $\nu(C=N)$ vibration suggests the coordination of one of the methine nitrogens and hence the formation of two dissimilar rings. The $\nu(C-O)$ phenolic shifts to a higher frequency and $\nu(Ti-N)$ and $\nu(Ti-O)$ vibrations appear as a result of complex formation.

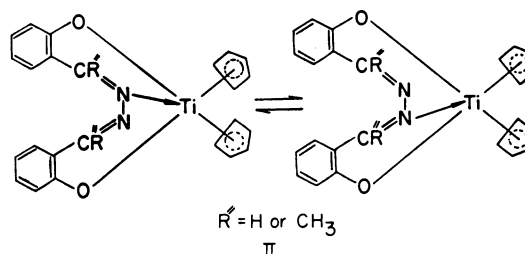
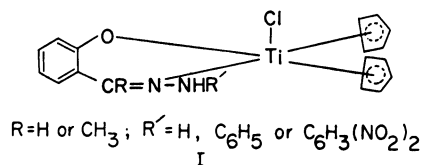
Proton Magnetic Resonance Spectra. All the hydrazone compounds give four different resonance signals corresponding to (i) C₆H₅ ring protons, which appear as a sharp singlet at *ca.* $\delta=6.40$, (ii) the $-CR=N-$ group proton(s), appearing at *ca.* $\delta=8.60$ (R=H); $\delta=3.00$ (R=CH₃), show a downfield shift as compared to the corresponding free hydrazone ligands *ca.* $\delta=8.40$ (R=H), $\delta=2.75$ (R=CH₃), indicating deshielding as a result of coordination through the nitrogen to titanium, (iii) aromatic protons, which appear as a multiplet at *ca.* $\delta=6.70-7.80$, also show a downfield shift as compared to the corresponding signals in the free ligands (observed at *ca.* $\delta=6.60-7.50$), further supporting the coordination of nitrogen of the azomethine group to the metal, (iv) the $-NH-$ and $-NH_2$ protons (*ca.* $\delta=4.85$ and $\delta=4.30$, respectively) appear at the same positions as observed for the free hydrazone ligands.

The ¹H NMR spectra of the azine complexes show three different resonance signals corresponding to (i) C₆H₅ ring protons, (ii) $-CR''=N-$ group proton(s), (iii) aromatic protons, and are quite similar to the ¹H NMR spectra of the hydrazone complexes.

Electronic Spectra. The electronic spectra of the complexes in chloroform exhibit a single band in the region 403—412 nm in accordance to the electronic configuration $(n-1)d^2, ns^0$ of titanium.¹¹⁾

Based on analytical data, general behaviour and physicochemical studies, structure I and II may be proposed to the hydrazone and azine derivatives under investigation, respectively.

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