

Synthesis and Characterization of Pseudohalides of Bis-Methylcyclopentadienyl Titanium(IV)

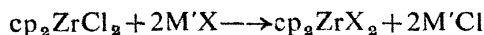
V. K. JAIN, N. K. BHATIA, K. C. SHARMA and B. S. GARG*

Department of Chemistry, University of Delhi, Delhi-110 007 (India)

Manuscript received 24 September 1979, accepted 30 November 1979

The pseudohalide complexes of the $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiX}_2$ type (where X=N₃, NCS, NCO and NCSe) have been prepared in aqueous medium ($p\text{H}\sim 2$) as well as in non-aqueous medium. These complexes have been characterized by elemental analyses, IR and NMR spectroscopy. These complexes are monomeric in benzene solution and non-electrolytes in nitrobenzene solution. On the basis of infrared spectroscopy, it has been shown that NCS, NCO and NCSe are N-bonded to the titanium atom. Thus these are true isothiocyanato, isocyanato and isoselenocyanato derivatives. The proton chemical shifts of these complexes have also been reported.

NUMBER of organometallic pseudohalides have been reported earlier¹⁻⁵. The two mixed halido-pseudohalido complexes of bis-cyclopentadienyl titanium(IV) namely $\text{cp}_2\text{Ti}(\text{Cl})\text{NCS}$ and $\text{cp}_2\text{TiCl}(\text{CN})$ were prepared⁶ in 1963 by the reaction of cp_2TiCl_2 and AgX in toluene (where X=CNS, CN). Jansen⁷ prepared $\text{cp}_2\text{Ti}(\text{NCS})_2$ a bis pseudohalido derivative of bis-cyclopentadienyl titanium(IV). The complex of the cp_2ZrX_2 type (where X=CNS, CNO) were prepared⁸⁻¹¹ by exchange reactions from cp_2ZrCl_2 in acetone, CH_2Cl_2 , C_6H_6 or nitrobenzene as follows :



M' = K or Ag

This paper deals with the isolation of pseudohalide complexes of the $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiX}_2$ type (where X=NCS, NCO, N₃ and NCSe) from $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$, by the reaction of sodium or potassium salts of appropriate pseudohalide in aqueous medium ($p\text{H}\sim 2$) or in acetone or THF. These complexes have been identified by their elemental analyses, melting points, IR and NMR spectroscopy.

Experimental

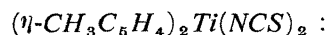
Reagents and Techniques :

KCNS (A.R. grade, B. D. H.) and NaN_3 (A. R. grade, B.D.H.) were used as supplied. KSeCN and KCNO were prepared as cited in the literature^{1,2}. All solvents used in the studies were properly dried. $(\eta\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2$ was prepared by the reaction of TiCl_4 with $\text{Na}(\text{CH}_3\text{C}_5\text{H}_4)$ as described by Reynolds and Wilkinson^{1,3}.

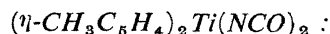
Preparation of complexes in aqueous solution :

A. Preparation of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{N}_3)_2$:

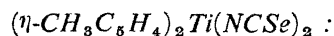
An aqueous solution of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$ was made by refluxing for 30 min a 0.5 g of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$ in water (50 cm³) (the pH of which was adjusted to (1.2-2) with hydrochloric acid). The clear solution so obtained was cooled to room temperature. To this aqueous solution was added an aqueous solution of NaN_3 (5 cm³ of 10% solution) dropwise. The orange precipitates obtained were extracted with (5 × 10 cm³) portions of CH_2Cl_2 . The combined extract was dried over anhydrous CaCl_2 and concentrated *in vacuo* to 20 cm³. Petroleum ether (60-80°) was added to the concentrate and the mixture was allowed to stand overnight. Bright orange crystals of the azido complex were obtained in 85% yield.



This complex was obtained by the method A, using (0.50 g) of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$ and 5 cm³ of 10% aqueous solution of KCNS. Maroon coloured crystals of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{NCS})_2$ were obtained in 70% yield.



This complex was obtained by the method A, using (0.50 g) of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$ and 4 cm³ of 10% aqueous solution of KCNO. Red orange coloured compound was obtained in 60% yield.



This complex was obtained by the method A, using (0.50 g) of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$ and 7 cm³

* Author to whom correspondence should be addressed.

of 10% aqueous solution of NaSeCN. Dark-brown coloured complex was obtained in 82% yield.

Preparation of complexes in non-aqueous medium :

B. Preparation of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{N}_3)_2$:

For preparing an azido complex (1.385 g, 0.005 mol) of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$ was refluxed with (0.65 g, 0.01 mol) of NaN_3 in 200 cm^3 of tetrahydrofuran for 5 hr, filtered after cooling it to room temperature. The filtrate was concentrated to ≈ 0 cm^3 *in vacuo*. To the concentrated solution was added 30 cm^3 of petroleum ether (60-80°) dropwise with constant stirring. The precipitates of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{N}_3)_2$ obtained was dried *in vacuo* to give <50% yield.

$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{NCS})_2$:

This complex was obtained in quantitative yield by method B, using (1.385 g, 0.005 mol) of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$ and (0.97 g, 0.01 mol) of KCNS in 200 cm^3 acetone for 4 hr.

$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{NCO})_2$:

This complex was obtained by method B, using (1.385 g, 0.005 mol) of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$ and (0.81 g, 0.01 mol) of KCNO in 200 cm^3 THF for 5 hr. The yield was <60%.

$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{NCS}_2)_2$:

This complex was obtained by method B, using (1.385 g, 0.005 mol) of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$ and (1.28 g, 0.01 mol) of NaSeCN in 200 cm^3 THF for 4 hr. The yield obtained was <50%.

Physical measurements :

The IR spectra were recorded in the region 4000-250 cm^{-1} on Perkin-Elmer Model 621 grating spectrometer calibrated with polystyrene film (Table 2).

The ^1H NMR spectra were recorded on Varian A-60 spectrometer at 30° using TMS as an internal standard at a sweep width of 500 Hz. The chemical shifts are believed to be accurate to ± 0.01 ppm (Table 3). The ^1H NMR spectrum for cyanato complex is shown in Figure 1.

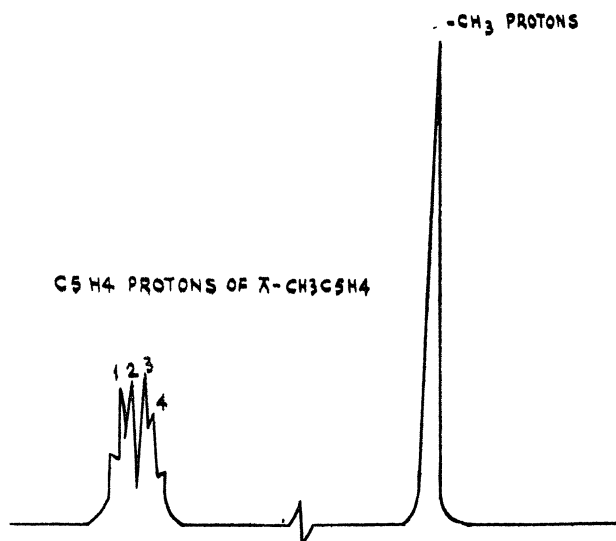


Fig. 1. ^1H NMR Spectrum of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{NCO})_2$ at 500 cps

Conductivity measurements were made in nitrobenzene at $30 \pm 0.5^\circ$ on a Beckmann RC-18A conductivity bridge. The cell constant was obtained by measuring the resistance of 0.02M KCl solution. C and H were got estimated microanalytically whereas Ti as TiO_2 gravimetrically. Elemental analyses, melting points, conductivity data, colours and molecular weights for these complexes are given in (Table 1).

Results and Discussion

The pseudohalide derivatives of the $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiX}_2$ type described in this paper have

TABLE 1—ELEMENTAL ANALYSES AND CONDUCTIVITY DATA FOR PSEUDOHALIDE DERIVATIVES $(\eta\text{-meC}_5\text{H}_4)_2\text{Ti}(\text{IV})$

Complex	Conductance data		C% Found (Calcd)	H% Found (Calcd)	Ti% Found (Calcd)	M.W. Found (Calcd)	m.p.°C and colour
	Λ $\text{ohm}^{-1} \text{cm}^2$ mole^{-1}	Molarity					
$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{N}_3)_2$	0.64	0.5	49.6 (49.7)	4.8 (4.8)	16.3 (16.5)	350 (289.9)	113-116°(d) orange
$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{NCS})_2$	0.52	0.5	52.0 (52.2)	4.4 (4.35)	14.8 (14.9)	380 (321.9)	220-222° maroon
$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{NCO})_2$	0.62	0.5	57.5 (57.9)	4.83 (4.8)	16.35 (16.5)	300 (290)	123-126°(d) red orange
$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{NCS}_2)_2$	0.33	0.5	40.1 (40.4)	3.4 (3.4)	11.2 (11.5)	385 (415.9)	219-223°(d) dark-brown

TABLE 2—VIBRATIONAL FREQUENCIES OF PSEUDOHALIDE DERIVATIVES OF $(\eta\text{-meC}_5\text{H}_4)_2\text{Ti(IV)}$

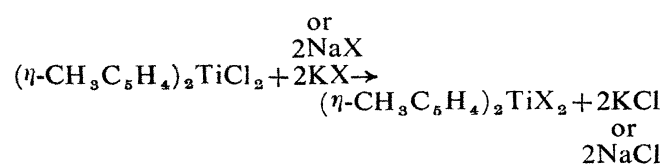
$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti(N}_3)_2$		$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti(NCS)}_2$		$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti(NCO)}_2$		$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti(NCSe)}_2$	
Band (cm^{-1})	Assignment	Band (cm^{-1})	Assignment	Band (cm^{-1})	Assignment	Band (cm^{-1})	Assignment
3090m	C-H stretching of ring	3085m	C-H stretching of ring	3105m	C-H stretching of ring	3095m	C-H stretching of ring
(1442m)	C-C (asymmetric ring breathing)	1445s	C-C (asymmetric ring breathing)	1440s	C-C (asymmetric ring breathing)	1441s	C-C (asymmetric ring breathing)
(1450m)	C-H (deformation in plane bending)	(1046m)	C-H (deformation in plane bending)	1020m	C-H (deformation in plane bending)	(1042s)	C-H (deformation in plane bending)
1030s	C-H (bending, out of plane deformation)	(1033sh)	C-H (bending, out of plane deformation)	812s	C-H (bending, out of plane deformation)	(1030m)	C-H (bending, out of plane deformation)
840vs	$\gamma_a(\text{NNN})$	843s	$\gamma(\text{CN})$	2208vs	$\gamma_a(\text{NCO})$	841vs	$\gamma(\text{CN})$
2020vs	$\gamma_s(\text{NNN})$	1980vs	$\gamma(\text{CS})$	1430sh	$\gamma_s(\text{NCO})$	2040vs	$\gamma(\text{CN})$
1340vs	$\delta(\text{NNN})$	843s	$\gamma(\text{NCS})$	632m, 600m	$\delta(\text{NCO})$	700s	$\gamma(\text{CSe})$
608sh, 600s	$\delta(\text{NNN})$	470m	$\gamma(\text{CH}_3\text{C}_5\text{H}_4 - \text{Ti} - \text{CH}_3\text{C}_5\text{H}_4)$	390s	$\gamma(\text{CH}_3\text{C}_5\text{H}_4 - \text{Ti} - \text{CH}_3\text{C}_5\text{H}_4)$	(420m) (393m)	$\gamma(\text{NCSe})$
428sh, 405s	$\gamma(\text{M} - \text{N})$	367s				350s	$\gamma(\text{CH}_3\text{C}_5\text{H}_4 - \text{Ti} - \text{CH}_3\text{C}_5\text{H}_4)$
350m	$\gamma(\text{CH}_3\text{C}_5\text{H}_4 - \text{Ti} - \text{CH}_3\text{C}_5\text{H}_4)$						

TABLE 3—PROTON CHEMICAL SHIFTS (Hz^1) FOR PSEUDOHALIDE COMPLEXES OF $(\eta\text{-meC}_5\text{H}_4)_2\text{Ti(IV)}$

No.	Complex	Deuteriochloroform solution	
		Ring protons ($\eta\text{-CH}_3\text{C}_5\text{H}_4$)	Methyl protons ($\eta\text{-CH}_3\text{C}_5\text{H}_4$)
1.	$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$	382.0, 380.2, 378.4 ^a	139.3
2.	$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti(N}_3)_2$	372.3, 370.3, 368.0, 365.7 ^b	130.6
3.	$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti(NCS)}_2$	384.0, 381.8, 377.0, 374.4 ^b	136.5
4.	$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti(NCO)}_2$	377.1, 374.7, 368.0, 365.6 ^b	132.1
5.	$(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti(NCSe)}_2$	386.7, 384.2, 379.4, 377.3 ^b	138.7

a = Position of three most intense peaks ;
b = Position of four most intense peaks.

been prepared from $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$ by the following reaction :



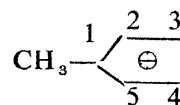
(where X = CNS, CNO, N₃, SeCN)

These complexes are soluble in organic solvent such as C₆H₆, CHCl₃, (CH₃)₂CO, CS₂ and nitrobenzene. Molecular weight determination in benzene as well as conductivity measurements in nitrobenzene indicate that these complexes are non-electrolytes and monomeric.

¹H NMR spectra :

In ¹H NMR spectra of these complexes two sharp signals in the ratio 6 : 8 are obtained i.e. (i) CH₃ protons of methylcyclopentadienyl (ii) a multiplet due to ring protons of methylcyclopentadienyl. The ¹H NMR spectra for CH₃C₅H₄

group in general forwardly interpretable on the basis of 1st order spin splitting approximations. In general the CH₃ group of methylcyclopentadienyl shields both the protons of C_{2,5} and C_{3,4} of the substituted ring, but the effect is more pronounced for protons at C_{2,5}



Adjacent and crossing coupling constant ($J_{2,3}$ and $J_{2,4}$ respectively) are very nearly equal and very small than the chemical shift difference between the two pairs of protons so that a unsymmetrical triplet is obtained (as shown for $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}_2$) in Table 3, but the pseudohalide group attached to Ti is sufficiently heavy to effect further the C_{2,5} and C_{3,4} protons and as a combined effect of CH₃ and pseudohalide groups a multiplet showing four most intense peaks is obtained as shown in Figure 1 (a representative spectrum for cyanato complex). Similar peaks were obtained in case of other complexes.

IR spectra :

The methylcyclopentadienyl group in these complexes is identified by C-H stretching band ($\sim 3100\text{ cm}^{-1}$), C-C (asymmetric ring breathing) ($\sim 1425\text{ cm}^{-1}$), C-H (deformation in plane bending) ($1125\text{-}1000\text{ cm}^{-1}$) and C-H (bending out of plane deformation) at $825\text{-}800\text{ cm}^{-1}$. This suggests centrally π -bonded $\text{CH}_3\text{C}_5\text{H}_4$ group in these complexes.

The azide, group in the azido complex is indicated by a characteristic asymmetric N-N-N stretching at 2020 cm^{-1} and a band at 600 cm^{-1} which is attributed to the doubly degenerate azide bending motion¹⁴. Other bands observed are symmetric N-N-N stretch at 1340 cm^{-1} and (Ti-N) stretch at 400 cm^{-1} . The similarity in the IR spectra with other metal azide¹⁴ suggests an ionic bonding between Ti atom and azide group in this complex.

In the thiocyanato complex the SCN group may coordinate to the titanium atom through N or S. Mitchell and Williams¹⁵ have shown that the C-N stretching frequencies are generally lower in M-NCS complexes than in the M-SCN complexes. The C-S stretching frequency may be used in distinguishing these two linkage isomers. For various complexes^{14,16,17} involving N bonding the C-S stretching frequency is around $780\text{-}850\text{ cm}^{-1}$ while for the complexes involving S-bonding is around $690\text{-}720\text{ cm}^{-1}$. The band at $780\text{-}860\text{ cm}^{-1}$ would be masked by the strong absorption at 843 cm^{-1} due to the (C-H) out of plane bending vibrations of the ring⁸. However, the absence of any band in the region $800\text{-}650\text{ cm}^{-1}$ together with the higher intensity of the 843 cm^{-1} band relative to $1046, 1033\text{ cm}^{-1}$ (C-H in plane bending) is a strong indication of the M-NCS structure in $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{NCS})_2$. Further NCS bending frequency is observed at 470 cm^{-1} .

In cyanato complex the CNO group may coordinate to titanium through O or N. So far only N-bonded complexes have been reported. For the metal cyanates (M-OC \equiv N), no fundamental frequency is expected around $1200\text{-}2000\text{ cm}^{-1}$, while metal isocyanates (M-N=C=O) have a pseudosymmetric stretch near 1400 cm^{-1} . $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{NCO})_2$ shows one band in this region at 1430 cm^{-1} thus the complex is true isocyanato complex bonded through N.

In selenocyanato complex the SeCN group may coordinate to a metal through N or Se. The CN stretching frequencies of the Se bonded complexes are in general higher than those of the N-bonded complexes. The C-Se stretching frequency is more useful in distinguishing the type of bonding.

The C-Se stretching frequency for N-bonded complexes appears at $690\text{-}620\text{ cm}^{-1}$ while for Se-bonded complexes around $540\text{-}510\text{ cm}^{-1}$ ¹⁸. The integrated intensity of the CN stretch is also useful in the identification of N-bonded and Se-bonded complexes¹⁹. Burmeister and Gysling^{20,21} prepared true linkage isomers $[\text{Pd}(\text{Et}_4\text{dien})(-\text{SeCN}/-\text{NCSe})]\text{BPh}_4$ where $(\text{Et}_4\text{dien}=\text{N},\text{N},\text{N}',\text{N}')$ tetra-ethyldiethylenetriamine) and observed that the CN, and CSe stretching frequencies of the Se-bonded isomers are around 2123 and 532 cm^{-1} respectively whereas those of the N-bonded are around 2090 and 816 cm^{-1} . In case of $(\eta\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Ti}(\text{NCSe})_2$ complex the bands are observed at 2040 and 700 cm^{-1} respectively indicating thereby N-bonded isomer.

Acknowledgement

The authors are thankful to the Chemistry Department, University of Delhi for providing necessary facilities to carry out the present work.

References

1. J. S. THAYER and R. WEST, *Adv. Organometal Chem.*, 1967, **5**, 169.
2. R. BUNSEN, *Ann. Chem.*, 1841, **37**, 23.
3. J. S. THAYER, *Organometal Rev.*, 1966, **1**, 157.
4. M. F. LAPPERT and H. PYSZORA, *Adv. Inorg. and Radio Chem.*, 1966, **9**, 133.
5. H. N. NORBURG, *Adv. Inorg. and Radio Chem.*, 1975, **17**, 231.
6. K. L. MCHUGH and J. O. SMITH, *U. S. Patent Appl.*, 1963, **3**, 242, 081.
7. A. JENSEN, *Proc. Int. Conf. Coord. Chem.*, 7th, 1972, p. 25.
8. R. S. P. COUTTS and P. C. WAILLES, *Aust. J. Chem.*, 1966, **19**, 2069.
9. R. S. P. COUTTS and P. C. WAILLES, *Aust. J. Chem.*, 1971, **24**, 1075.
10. E. SAMUEL, *Bull. Soc. Chim. Fr.*, 1966, p. 3548.
11. J. I. BURMEISTER, E. A. DEARDORFF, A. JENSEN and V. H. CHRISTIANSEN, *Inorg. Chem.*, 1970, **9**, 58.
12. J. C. BAILER, JR (Ed), *Inorg. Synth.*, 1950, **2**, 86 and 186.
13. L. T. REYNOLDS and G. WILKINSON, *J. Inorg. Nuclear Chem.*, 1959, **9**, 86.
14. D. A. DOWS, E. WHITE and G. C. PIMENTAL, *J. Chem. Phys.*, 1958, **6**, 187.
15. P. C. H. MITCHELL and R. J. P. WILLIAMS, *J. Chem. Soc.*, 1960, 1912.
16. H. A. PAPA ZIAN, *J. Chem. Phys.*, 1961, **34**, 1614.
17. S. AERLAND, J. CHATT and N. R. DAVIES, *Quart. Rev.*, 1958, **12**, 265.

18. C. PECILE, A. TURCO and G. PIZZOLLOTO, *Ric. Sci.* 1961, **31**, 2A, 247.
19. J. L. BURMEISTER and L. E. WILLIAMS, *Inorg. Chem.*, 1966, **5**, 1113.
20. J. L. BURMEISTER and H. J. GYSLING, *Inorg. Chim. Acta*, 1967, **1**, 100.
21. J. L. BURMEISTER and H. J. GYSLING, *Chem. Commun.*, 1967, 543.