

SUBSTITUENT EFFECTS IN CYCLOPENTADIENYL DERIVATIVES OF TITANIUM AND ZIRCONIUM

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SUMMARY

Study of ring-substituted π -cyclopentadienyl dichlorides of Ti and Zr shows that the metal-to-ring and metal-to-chloride bonds are sensitive to the donor and acceptor character of the substituent. The preparation of new compounds is reported, namely $\text{Cp}(\text{Ind})\text{TiCl}_2$ (I), $(\text{IndH}_4)\text{TiCl}_3$ (II) and the oxides $[(\text{IndH}_4)\text{TiCl}_2]_2\text{O}$ (III) and $[(\text{IndH}_4)\text{TiClO}]_4$ (IV) derived from (II), and their NMR spectra are given. The previously reported ABC spectrum of the C_5 ring protons in $[(\text{IndH}_4)_2\text{ZrCl}]_2\text{O}$ (V) is further confirmed by spin decoupling experiments. The nonequivalent environments of these protons is suggested as a possible explanation of their peculiar NMR behaviour.

INTRODUCTION

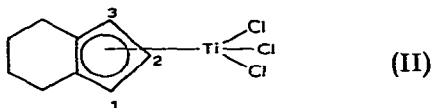
It is now well established that π -cyclopentadienyl derivatives of Ti, Zr and Hf^{IV} have a structure in which the two rings bonded to the metal are at an angle to each other ^{1,2} ($59^\circ \pm 3^\circ$ in Cp_2TiCl_2). The present work was carried out with a view to studying the following: chemical and spectroscopic behaviour of those derivatives of group IVA elements in which a substituent is introduced into the ring (as in methylcyclopentadienyl, indenyl and 4,5,6,7-tetrahydroindenyl derivatives)*; chemical behaviour with respect to the influence of electron-donating or withdrawing substituents on the stability of the complex, and spectroscopic (mainly NMR) behaviour with respect to the chemical shift and coupling modes of the C_5 ring protons, and in some compounds the possible interaction between the two rings bonded to the same metal³.

We have previously reported⁵ that NMR spectra of the dimeric Zr oxides $(\text{L}_2\text{ZrCl})_2\text{O}$, where $\text{L} = \text{MeC}_5\text{H}_4$, and (IndH_4) exhibit coupling patterns different from those expected from a π -bonded complex. This question deserved further investigation, and attempts to find an interpretation incited us to prepare oxides of Ti compounds having the same ligands in order to compare their NMR spectra.

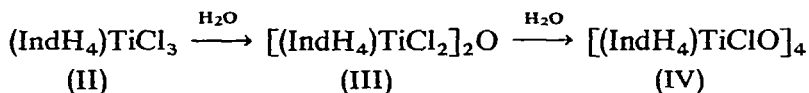
RESULTS AND DISCUSSION

Derivatives having the general formula L_2MCl_2 ($\text{M} = \text{Ti}, \text{Zr}$) have been studied, and their preparation has been described earlier⁴⁻⁵. In addition, we report here

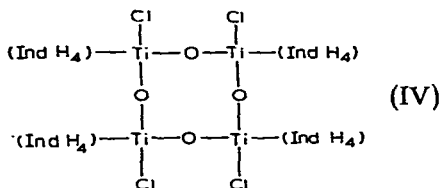
* Successively abbreviated as (MeC_5H_4) , Ind and (IndH_4) ; Cp stands for the cyclopentadienyl radical.



the preparation of $(\text{IndH}_4)\text{TiCl}_3$ (II) a new complex obtained by the action of gaseous chlorine on solutions of $(\text{IndH}_4)_2\text{TiCl}_2$ in CCl_4 . This compound can be easily hydrolysed in two steps as follows:



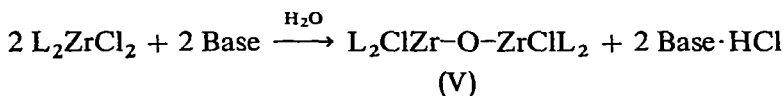
The intermediate compound (III) was detected in solution from its NMR spectrum but could not be isolated; (IV) crystallises as bright yellow needles. Oxide (IV) contains the linear Ti-O-Ti bond which shows a characteristic strong IR band at 800 cm^{-1} . Measurements of molecular weight have proved that it is a tetramer, presumed to have the following structure (isomers are also possible):



Analogous derivatives with MeC_5H_4 have also been obtained. The Zr homologues of (II) could not be obtained, since the action of Cl_2 on $(\text{IndH}_4)_2\text{ZrCl}_2$ resulted in the complete breakdown of the molecule.

The chemical properties, such as stability towards decomposition and hydrolysis of $\text{L}'\text{MCl}_2$ [$\text{L}' = (\text{MeC}_5\text{H}_4)$, Ind and (IndH_4)] can be roughly correlated to the nature of the substituent on the ring when compared to the unsubstituted Cp_2MCl_2 compounds.

Thus, in the indenyl complexes, the phenyl ring behaves as an electron-withdrawing substituent towards the cyclopentadienyl ring bonded to the metal. These complexes decompose readily in polar organic solvents with cleavage of both metal-to-ring bonds, in the same manner as diindenyl compounds of Fe and Ru⁶. The phenyl ring, upon saturation, behaves as an electron-releasing substituent, resulting in a considerably enhanced stability of the tetrahydroindenyl compounds, even more than the cyclopentadienyl homologues. This is fairly well illustrated by the reactions whereby L_2ZrCl_2 compounds hydrolyse to give the dimeric oxides $(\text{L}_2\text{ZrCl}_2)_2\text{O}$:



Thus, while a weak base hydrolyses the cyclopentadienyl derivative, more drastic conditions like pyridine in hot methanol are needed to convert $(\text{MeC}_5\text{H}_4)_2\text{ZrCl}_2$ to the oxide $[(\text{MeC}_5\text{H}_4)_2\text{ZrCl}]_2\text{O}$ and diethylamine (a stronger base) in moist ether to completely transform $(\text{IndH}_4)_2\text{ZrCl}_2$ into $[(\text{IndH}_4)_2\text{ZrCl}]_2\text{O}$.

A similar though not identical trend is shown by the corresponding Ti deriva-

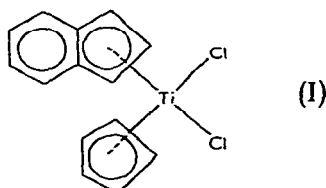
tives. Addition of a base to an aqueous solution of Cp_2TiCl_2 cleaves the metal-cyclopentadienyl bond⁷, whereas L_2TiCl_2 compounds are completely insoluble in boiling water and remain unaltered by the action of strong aqueous bases.

Cp_2TiCl_2 is readily reduced in THF or acetone by zinc dust to green paramagnetic $\text{Cp}_2\text{Ti}^{\text{III}}\text{Cl}$ derivative which, upon careful oxidation, yields the crystalline orange oxide $(\text{Cp}_2\text{TiCl})_2\text{O}$ (ref. 8). THF or acetone solutions of L_2TiCl_2 are very slowly attacked by zinc dust; the reaction is instantaneous only in solvents such as diethyl, dibutyl ketone or ethyl acetate, leading to green or blue paramagnetic solutions. Upon slow oxidation these turn orange. However, all attempts to isolate the oxide presumed to be present in the solution have failed, and treatment with HCl does not give back the starting dichloride; consequently, $(\text{L}_2\text{TiCl})_2\text{O}$ could not be isolated.

From the preceding observations, it follows that increasing the donor substituent on the Cp ring renders the metal-chloride bond in substituted cyclopentadienyl derivatives of Ti and Zr^{IV} more resistant to reduction and hydrolysis. Apparently, the M-Cl bond becomes more electron populated, a part of the excess charge from the substituent being transmitted through the ring and the metal.

CpIndTiCl₂

Derivatives in which two different rings are bonded to the same metal such as $\text{Cp}(\text{MeC}_5\text{H}_4)\text{TiCl}_2$ and CpIndFe have already been mentioned^{3,9}. We report here the preparation of a new Ti derivative, CpIndTiCl_2 , a dark brown crystalline solid



obtained by the action of IndNa on CpTiCl_3 in THF. It is more stable in organic solvents than is the diindenyl homologue, although cleavage of the titanium-indenyl bond takes place upon slow oxidation, leaving the yellow $(\text{CpTiCl}_2)_2\text{O}$ as an end product. This preferential bond breaking is another example of the electron-withdrawing effect of the phenyl ring which is responsible for the fragility of the titanium-indenyl bond.

¹H NMR spectra

A survey of the ¹H NMR spectra of the π -complexes investigated above provides an approximate picture of:

- (a). Electron density of the ring as indicated by chemical shift values.
- (b). Chemical environments of the protons as indicated by their coupling modes.

(a). It is now well recognised that values of proton chemical shifts in aromatic compounds give information about the π -electron density of the carbon to which the proton is bonded. Study of the values of ring proton chemical shifts (Table 1) shows that resonance of the ring protons of all MeC_5H_4 and IndH_4 derivatives lies upfield as compared to the shift in the cyclopentadienyl derivative; resonance of C_5 protons is shifted downfield for the indenyl moiety in derivative (I) (spectra of diindenyl compounds could not be obtained due to poor solubility or decomposition in polar sol-

TABLE I

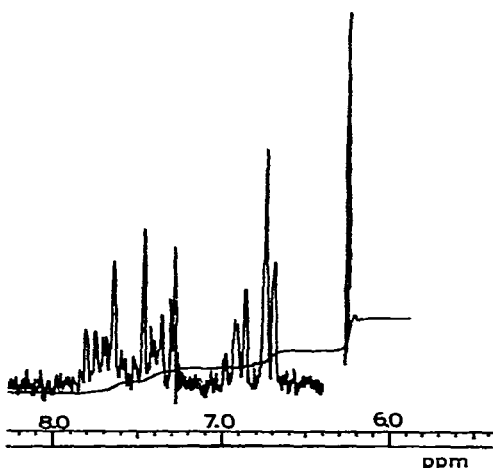
PROTON CHEMICAL SHIFTS (AT 60 MHz) OF SOME SUBSTITUTED CYCLOPENTADIENYL TITANIUM DERIVATIVES

Compound	Solvent	δ (ppm)
CpIndTiCl ₂	CDCl ₃	
Cp		6.20
C ₅ ring in C ₉ H ₇		6.86 triplet
		6.66 doublet
C ₆ ring in C ₉ H ₇		7.2 to 7.9 multiplet
Cp ₂ TiCl ₂	CD ₃ COCD ₃	6.61
(MeC ₅ H ₄) ₂ TiCl ₂ ^a	CD ₃ COCD ₃	6.31 triplet
		6.56 triplet
(IndH ₄) ₂ TiCl ₂ ^a	CDCl ₃	6.30 triplet
		5.78 doublet

^a C₅ ring signals.

vents). This can be interpreted as an increased shielding of the ring protons in the first case and decreased shielding in the second case, brought about by donor or acceptor substituents. This argument is supported by the chemical evidence discussed above: the M-Cl bond is indirectly reinforced by increased electron density on the rings, and the metal-to-ring bonding is weakened by electron-withdrawing substituents (easy cleavage of M-Ind bond in CpInd and diindenyl complexes).

(b). Coupling between protons is related to their magnetic equivalence. The sharp angle formed by the two rings bonded to the metal would permit an interaction between them when one or more of their protons is replaced by a bulkier group. This was demonstrated for Cp(MeC₅H₄)TiCl₂ and Cp(C₅Me₅)TiCl₂³; their spectra show that the signal of the nonsubstituted ring is split due to *contact* of two of its protons with a methyl group of the other ring. However, no such interaction seems to exist in the case of CpIndTiCl₂; its NMR spectrum (of a solution in CDCl₃) shows the usual singlet for the Cp protons at 6.20 ppm and the expected AB₂ spectrum for the three indenyl protons on positions 1, 2, 3 besides the multiplet due to the phenyl ring

Fig. 1. NMR spectrum of CpIndTiCl₂ in CDCl₃.

(Fig. 1). The NMR spectrum of CpIndFe^9 is quite similar except for the relative chemical shifts of the protons 1,3 (doublet) whose signal lies at a lower field than 2 (triplet).

An AB_2 pattern for the C_5 protons was found also for the tetrahydroindenyl derivatives (II), (III) and (IV) (Table 2).

TABLE 2

Compound	Doublet (H_1, H_3) (δ)(ppm)	Triplet (H_2) (δ)(ppm)
$(\text{IndH}_4)\text{TiCl}_3$	6.65	7.03
$[(\text{IndH}_4)\text{TiCl}_2]_2\text{O}$	6.45	6.83
$[(\text{IndH}_4)\text{TiClO}]_4$	6.23	6.62

This proves that in all these compounds, protons 1 and 3 have identical environments and are therefore magnetically equivalent.

An unexpected behaviour is shown by $[(\text{IndH}_4)_2\text{ZrCl}]_2\text{O}$; it gives an ABC-type spectrum for the C_5 protons⁴ which consists of three well-separated triplets. That it is a true ABC spectrum was confirmed by theoretical analysis and by the following measurements:

- (1). At 100 MHz no change is observed except for the δ values.
- (2). Spin decoupling of each one of the three protons gives two doublets for the two remaining protons (Fig. 2).

These measurements gave the following J values: $J_{12} = J_{23} = 2.2$ Hz and $J_{13} = 3.15$ Hz.

It is noteworthy that no change in the spectrum was observed at temperatures between -70° and 150° .

Although no unequivocal interpretation of this anomaly can be derived from the available data, one can safely suggest from a study of the molecular model that the heavily crowded environments of the metal atom hinder the rotation of the rings

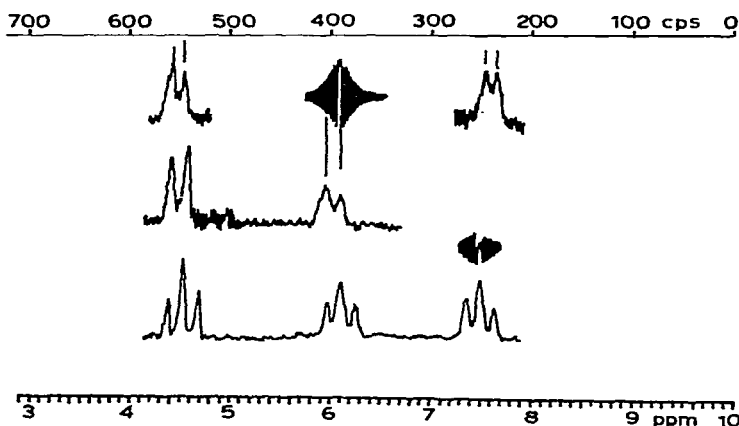


Fig. 2. Spin decoupling figures at 100 MHz of two of the three C_5 ring protons in $[(\text{IndH}_4)_2\text{ZrCl}]_2\text{O}$.

around the metal–ring bond axis. In this quasi-static configuration, protons 1 and 3 occupy nonequivalent sites (one of them *facing* the chlorine atom but not the other). A very similar behaviour was shown by the corresponding hafnium derivative.

The same argument is valid also to explain the difference observed in the NMR spectra of $(\text{MeC}_5\text{H}_4)_2\text{ZrCl}_2$ and $[(\text{MeC}_5\text{H}_4)_2\text{ZrCl}]_2\text{O}$ which show a symmetrical A_2B_2 spectrum⁴ for the former and a complex ill-defined spectrum for the latter.

IR spectra

IR spectra of Ind_2MCl_2 in the C–H bending region show that the indenyl moiety is of high symmetry compatible with π -bonding to the metal. It is noteworthy that in the spectrum of CpIndTiCl_2 the strong band at 820 cm^{-1} [$\gamma(\text{C-H})$] and the medium band at 1000 cm^{-1} lie at frequencies very close to those in the spectrum of Cp_2TiCl_2 ; CpIndTiCl_2 : a strong band at 830 cm^{-1} , medium bands at 850, 870, 1015 and 1020 cm^{-1} ; Cp_2TiCl_2 : a strong band at 820 cm^{-1} , medium bands at 870, 1010 and 1030 cm^{-1} .

This shows that the bending vibrations [γ and $\delta(\text{C-H})$] of the C_5H_5 ring and of the C_5 ring in C_9H_7 have approximately the same frequency and intensity (the strong band at 750 cm^{-1} in the indenyl compounds is due to the phenyl ring). It proves also that the local ring symmetry is conserved in the disymmetrical molecule (I).

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