

## X-RAY ELECTRON SPECTROSCOPY OF SOME ORGANOSCANDIUM COMPOUNDS

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### Summary

X-ray electron spectra of  $(C_5H_5)_2ScCl$  and  $C_5H_5ScC_8H_8$  are reported and compared with those of the titanium analogues. The results show that the charges on the  $C_5H_5$  ligands in the Ti and Sc compounds do not differ significantly, whereas the  $C_8H_8$  ligand is more negatively charged in the Sc than in the Ti compound.

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### Introduction

Organoscandium compounds have been known since the preparation of  $(C_5H_5)_3Sc$  by Wilkinson and Birmingham [1]. However, the bonding in such compounds has been studied only in the case of  $(C_5H_5)_3Sc$ . The bonding between the metal and the ligands was first believed to be wholly ionic [1], but later, Atwood and Smith [2] showed from crystal structure data that there is at least a small covalent contribution to the bonding.

In this paper we describe the results of a study of the bonding in the compounds  $(C_5H_5)_2ScCl$  and  $C_5H_5ScC_8H_8$  by means of X-ray electron spectroscopy (ESCA).

### Experimental

$(C_5H_5)_2ScCl$  and  $C_5H_5ScC_8H_8$  were prepared as described in the literature [3,4]. Sc metal and  $Sc_2O_3$  were obtained commercially. ESCA measurements were performed with an A.E.I. ES-200 photoelectron spectrometer, using Mo- $K_\alpha$  radiation (1253.6 eV).  $(C_5H_5)_2ScCl$  and  $C_5H_5ScC_8H_8$  were inserted into the vacuum chamber in a capillary and sublimed onto the copper sample holder, which was cooled to  $-60^\circ C$ . During the measurements the vacuum was about  $10^{-8}$  Torr.  $Sc_2O_3$  was measured as a thin layer on tape, and Sc metal as a thin sheet after cleaning by argon bombardment. In spite of this, the spectra obtained of Sc metal were always superimposed on the spectrum of  $Sc_2O_3$ . We obtained

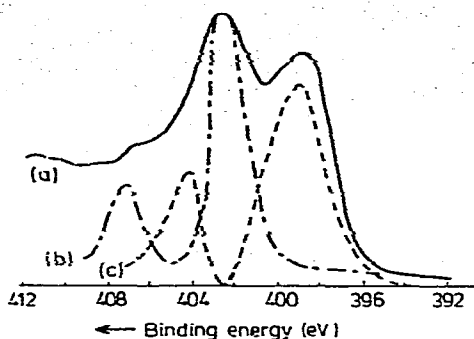


Fig. 1. Narrow scan ESCA spectrum of Sc metal: (a) spectrum observed from Sc sheet; (b) spectrum of  $\text{Sc}_2\text{O}_3$ ; (c) spectrum of Sc (a - b).

a reliable ESCA spectrum of the metal by subtracting the  $\text{Sc}_2\text{O}_3$  spectrum, as shown in Fig. 1.

### Results and discussion

The binding energies of the  $2p$  levels of Sc in the measured compounds are given in Table 1. If we assume charges of +3 and zero for  $\text{Sc}_2\text{O}_3$  and Sc metal, respectively, the charges of the metal in the other compounds can be estimated by linear interpolation. This approximation leads to somewhat overestimated charges, mainly due to some covalency in the Sc—O bond (according to Pauling [5] the Sc—O bond is about 70% ionic), but it is a reasonable way of revealing trends in the charges on atoms in related compounds [6], for instance in  $(\text{C}_5\text{H}_5)_2\text{TiCl}$  and  $\text{C}_5\text{H}_5\text{TiC}_8\text{H}_8$  [7,8].

Groenenboom [7,8] estimated a charge of +1.4 for Ti in  $(\text{C}_5\text{H}_5)_2\text{TiCl}$ . From ESCA [7] and other experiments [9] it was concluded that the charge on the five-membered rings in the compounds  $\text{C}_5\text{H}_5\text{MC}_7\text{H}_7$  ( $M = \text{Ti}, \text{V}, \text{Cr}$ ) is almost the same, being 0.3–0.4 electrons. The charges found for Sc and Ti in the compounds  $(\text{C}_5\text{H}_5)_2\text{MCl}$  are almost the same (+1.5 and 1.4 respectively). This means, that, again, the charge on the five-membered rings is not changed substantially. The slight difference of 0.1 charge unit can be explained using Pauling's electronegativity table [5], which predicts a somewhat more negatively charged chlorine atom in the Sc—Cl bond.

TABLE 1  
CORE LEVEL BINDING ENERGIES IN Sc COMPOUNDS (in eV)

Compound	Sc		C	Cl		Oxidation state
	$2p_{3/2}$	$2p_{1/2}$	1s	$2p_{3/2}$	$2p_{1/2}$	
$(\text{C}_5\text{H}_5)_2\text{ScCl}$	400.9	405.8	284.3	199.0	200.3	+1.5
$\text{C}_5\text{H}_5\text{ScC}_8\text{H}_8$	400.1	405.0	284.7			+0.9
$\text{Sc}_2\text{O}_3$	402.8	407.5				+3.0 <sup>b</sup>
Sc	399.0	403.8 <sup>a</sup>				+0.0 <sup>b</sup>

<sup>a</sup> Derived from Fig. 1. <sup>b</sup> Assumed values.

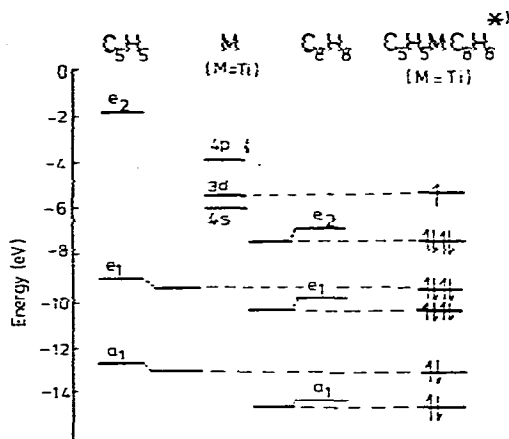


Fig. 2. Qualitative MO scheme of the bonding in  $C_5H_5MC_8H_8$ . \* Values taken from ref. 8.

As far as the metal— $C_5H_5$  bond is concerned, no differences are expected between  $(C_5H_5)_2MCl$  on the one hand and  $C_5H_5MC_8H_8$  on the other. Therefore, any difference found between charges on Sc and Ti in the compounds  $C_5H_5MC_8H_8$  can be ascribed to differences in charge of the eight-membered rings. For Sc we found an oxidation state of +0.9, whereas for Ti an oxidation state of +0.4 was observed [8]. From the latter value it was concluded that the charge on the eight-membered ring in  $C_5H_5TiC_8H_8$  is almost zero. Evidently, in  $C_5H_5ScC_8H_8$  the eight-membered ring carries a charge of about 0.5 electrons.

Our results can be interpreted by qualitative MO considerations, in the way proposed for the compounds  $C_5H_5MC_7H_7$  [9], for which the negative charge of the seven-membered ring increases in the series  $M = Cr \rightarrow V \rightarrow Ti$ . (see Fig. 2.)

Because of the increase in the energy of the metal 3d levels in going from Ti to Sc [10] the bonding molecular orbitals of  $\delta$  symmetry (consisting of  $e_2$  orbitals of the eight-membered ring and metal  $3d_{x^2-y^2}$  and  $3d_{xy}$  orbitals) have more ligand character in the Sc compound. Since the contributions of the metal and the ring to these MO's are of the same order, changes in these contributions are reflected in the charges upon the metal and the  $C_8H_8$  ring. More ligand character in the Sc case causes a substantial flow of electrons from the metal to the  $C_8H_8$  ligand.

The MO's of  $\delta$  symmetry are of major importance for the bonding of the early transition metals and  $C_8H_8$  (or  $C_7H_7$ ) rings [11]. For bonding between the metal and a five-membered ring the MO's of  $\delta$  symmetry are of minor importance; the most important contribution comes from the MO's of  $\pi$  symmetry (consisting of ligand  $e_1$  and metal  $3d_{xz}$  and  $3d_{yz}$  orbitals). Evans et al. [11] concluded from PES measurements, that these  $\pi$  orbitals have predominant ligand character. This is why an increase of the metal 3d energy has a much smaller effect on the charge of a  $C_5H_5$  ring than on the charge of a  $C_8H_8$  (or  $C_7H_7$ ) ring.

We conclude that the bonding in  $(C_5H_5)_2ScCl$  and  $C_5H_5ScC_8H_8$  is essentially the same as in the titanium analogues. The relatively low charges on Sc in the compounds indicate, that the Sc-ring bonds are appreciably covalent in character.

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## References

- 1 G. Wilkinson and J.M. Birmingham, *J. Amer. Chem. Soc.*, **87** (1956) 42.
- 2 J.L. Atwood and K.D. Smith, *J. Amer. Chem. Soc.*, **95** (1973) 1488.
- 3 R.S.P. Coutts and P.S. Wailes, *J. Organometal. Chem.*, **25** (1970) 117.
- 4 A. Westerhof and H.J. de Liefde Meijer, *J. Organometal. Chem.*, **116** (1976) 319.
- 5 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, New York, 1960.
- 6 C.D. Cook, K.Y. Wan, U. Gelius, K. Hamrin, G. Johansson, E. Olsson, H. Siegbahn, C. Nordling and K. Siegbahn, *J. Amer. Chem. Soc.*, **93** (1971) 1904.
- 7 C.J. Groenenboom, G. Sawatzky, H.J. de Liefde Meijer and F. Jellinek, *J. Organometal. Chem.*, **79** (1974) C4.
- 8 M. Vlieg, C.J. Groenenboom, H.J. de Liefde Meijer and F. Jellinek, *J. Organometal. Chem.*, **94** (1975) 67.
- 9 C.J. Groenenboom, H.J. de Liefde Meijer and F. Jellinek, *J. Organometal. Chem.*, **69** (1974) 235.
- 10 H. Basch, A. Viste and H.B. Gray, *J. Chem. Phys.*, **44** (1966) 10.
- 11 S. Evans, J.C. Green, S.E. Jackson and B. Higginson, *J. Chem. Soc. Dalton Trans.*, **3** (1974) 304.