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BONDING STUDIES OF TRANSITION METAL COMPLEXES

I. He(I) PHOTOELECTRON SPECTRA OF d^0 SILYLMETHYL AND NEOPENTYL DERIVATIVES OF GROUP IVA METALS

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Summary

The He(I) photoelectron spectra of the compounds MR_4 and $M'R'_4$ (M = Ti, Zr, or Hf; M' = M, Ge, or Sn; R = Me_3CCH_2; R' = Me_3SiCH_2) have been measured. From these and published data the spectra have been assigned in terms of a localised bond model assuming a tetrahedral MC_4 framework. The highest occupied molecular orbital (MO) lies in the range 8 - 9 eV and is assigned to σ(M—C) or σ(M′—C). For isoleptic transition metal alkyls, the highest MO is very insensitive to the nature of the central metal, while for corresponding Group IVB complexes the expected decrease in first ionisation potential (IP) due to progressive decrease in electronegativity with atomic number is observed. Small inductive effects of the ligands account for the different IP's of silylmethyl compounds compared with neopentyl derivatives. Observed stability trends are not related to ground state electronic effects.

Broadening is observed for the first band in the zirconium and hafnium neopentyls and this is ascribed to a distortion of the MC_4 framework to D_{2d}.

Introduction

This series derives in part from our earlier interest in bonding problems of boron and Group IVB compounds [1]. As in those studies, our objectives are to determine experimentally electronic energy levels and standard heats of formation; by suitable choice of series of compounds to assign the energy levels to particular molecular orbitals (MO's), and from the values of ΔH_f^0 to derive thermochemical bond energy terms, E. Trends in MO shifts and/or E may correlate with chemically significant parameters. Experimental methods which are relevant to these objectives are He(I) photoelectron (PE) spectra and calorimetry.

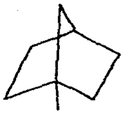
The compounds which will be examined initially, and reported in this and subsequent papers, are the volatile binary (isoleptic) alkyls [$MAlk_n$ where Alk is $R^1 = Me_3CCH_2$, $R^2 = Me_3SiCH_2$, $R^3 = (Me_3Si)_2CH$, R^4 = 1-norbornyl, R^5 = 1-camphenyl, R^6 = 4-camphenyl] and amides $M(NR^7_2)_n$ (R^7 = Me or Me_3Si) of the transition metals. Our interest in them derives from previous synthetic studies [2,3]. At present, they form the most extensive series of volatile transition metal complexes available. Stability in the gas phase is, of course, a necessary pre-requisite for PE spectroscopy; their high local symmetry also makes them suitable for PE study.

Until 1970 the only well-characterised transition metal isoleptic alkyl was $TiMe_4$, which decomposes at or near $-70°$ [4]. Recently, however, stable isoleptic alkyls of the early transition metals have been described (Table 1, R^1 to R^6 are as defined above). The stability of these compounds was attributed to kinetic factors, and specifically to decomposition transition states of higher-than-usual free energy. It is clearly relevant also to examine ground state effects. This paper addresses itself to that problem for the d^0 complexes MR^1_4 and MR^2_4 (M = Ti, Zr, or Hf) and their highest occupied MO's. These, being closed

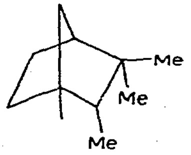
TABLE 1

STABLE ISOLEPTIC TRANSITION METAL ALKYLS : $R^1 = Me_3CCH_2$, $R^2 = Me_3SiCH_2$.

$R^3 = (Me_3Si)_2CH$, R^4 =



R^5 =



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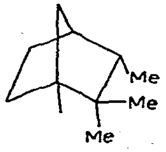
R^6 =



Compound type	Examples	Ref.
$(MAlk)_n$	d^{10}: $(CuR^2)_4$	8
	d^0 : YR^3_3	9
$(MAlk_3)_n$[a]	d^3 : CrR^3_3	9
	CrR^6_3	5
$(MAlk_3)_n$[a]	d^0 : YR^3_3	9
	d^3 : CrR^3_3	9
	d^3 : $(MoR^2_3)_2$, $(WR^1_3)_2$	10 (R^1)
	$(MoR^1_3)_3$	13
$MAlk_4$	d^0 : MR^1_4, MR^2_4,	12 and 13 (not Hf) (R^1),
	(M = Ti, Zr, or Hf)	11 (R^2)
	MR^4_4	5
	(M = Ti, Zr, or Hf)	
$MAlk_4$	d^1 : VR^2_4	10
	VR^4_4	5
$MAlk_4$	d^2 : CrR^1_4 CrR^2_4	14 (R^1), 10 (R^2)
	CrR^4_4 CrR^5_4	5
$MAlk_4$	d^3 : MnR^4_4	5
$MAlk_4$	d^4 : FeR^4_4	5
$MAlk_4$	d^5 : CoR^4_4	5
$MAlk_6$	d^0 : WMe_6	16

[a] The d^0 compounds ScR^1_3, ScR^2_3, YR^1_3, and YR^2_3 are also known [15], but these have 2 mol of THF as co-ligand.

shell systems, lend themselves to clearer interpretation than those of open-shell systems, where Koopman's theorem may not apply. Simple organic derivatives which may be regarded as the parent compounds, Me_4C and Me_4Si, have been studied by PE spectroscopy [6].

The chemical facts which require interpretation seem to be the following. (*i*) Isoleptic transition metal alkyls are generally less stable than those of Main Group elements. (*ii*) The effect of changes of ligand upon transition metal alkyl stability is profound, and the latter generally decreases in the order:

$Me_3CCH_2 \approx Me_3SiCH_2 \approx$  $\gg Me > Et$

For Main Group element analogues, there is no profound ligand dependance.

Apart from interpretation, it is obviously necessary more clearly to define "stability" in the above context: in terms of orbital energies, bond strengths, and thermal decomposition mechanisms. At present, the only available data relate to MC_4 stretching modes, which suggest that bond strengths defined in these terms do not differ widely in the following compounds [$\nu_{as}(MC_4)$, cm^{-1} in parentheses]: $TiR^1{}_4$ (540), $TiR^2{}_4$ (500), $ZrR^1{}_4$ (530), $ZrR^2{}_4$ (475), $HfR^1{}_4$ (536), $HfR^2{}_4$ (470), $SnR^1{}_4$ (590) [12], and $SnR^2{}_4$ (510) [10]. These values may be compared with 532 cm^{-1} for $SnMe_4$ [17].

This paper reports on the He(I) PE spectra of the tetraneopentyl, and (trimethylsilyl)methyl derivatives of Ti, Zr, Hf, and, for comparison, of Ge and Sn. A similar study on $(Me_3SiCH_2)_4M$ (M = Cr, Sn, or Pb) and $(Me_3CCH_2)_4Cr$ has recently been reported [7]; the results are consistent with and complementary to those here reported.

An attempt was made to record the PE spectrum of $TiMe_4$, by evaporating the vapour from a cold trap into the inlet system of the spectrometer; decomposition of the vapour, by exposure to the photon beam, afforded a film of metallic titanium on the probe.

Experimental

The compounds were synthesized by published procedures [11,12]. The purities of the compounds were checked by the usual spectroscopic methods,

TABLE 2

ENERGIES (eV) OF THE THREE HIGHEST OCCUPIED MO'S OF M $(CH_2CMe_3)_4$

M in M $(CH_2CMe_3)_4$						Assignment	Me_4C [b]
Ti	Zr	Hf	Ge	Sn	Cr [a]		
					7.2_5	d-Electrons of Cr	
8.3_3	8.3_3	8.5_1	9.0_1	8.5_8	8.3_7	σ (M—C)	
11.3_5	11.2_8	11.4_0	10.2_8	11.1_6	11.0	(C—C)	11.3 [c]
12.5_9	12.5_0	12.5_4	12.2_5	12.3_7	12.2	(C—H)	12.5

[a] Ref. 6. [b] Ref. 7. [c] Mean value.

TABLE 3

ENERGIES (eV) OF THE THREE HIGHEST OCCUPIED MO'S OF $M(CH_2SiMe_3)_4$

M in $M(CH_2SiMe_3)_4$						Assignment	Me_4Si [b]
Ti	Zr	Hf	Sn [a]	Pb [a]	Cr [a]		
					7.2_5	*d*-Electrons of Cr	
8.5_8	8.6_4	8.5_8	8.7_1	8.1_4	8.6_9	σ (M—C)	
				8.8_6			
10.4_6	10.2_8	10.2_7	10.3	10.3	10.4	(Si—C)	10.6
13.3_5	13.2_2	13.3_6	13.2	13.2	13.6	(C—H)	13.1/14.0

[a] Ref. 6. [b] Ref. 7.

and all the compounds were either resublimed (neopentyls) or distilled [(trimethylsilyl)methyls] prior to use.

Spectra were recorded on a PS 16 PE spectrometer; sample temperatures varied from room temperature to 50°. The sample and inlet tubes were heated uniformly to admit a constant pressure of sample. The spectra were calibrated using rare gases. The instrumental resolution (f.w.h.m. $^2P_{3/2}$ Argon) was 40 eV and the estimated accuracy of the peak positions given in Tables 2 and 3 is better than ± 0.1 eV.

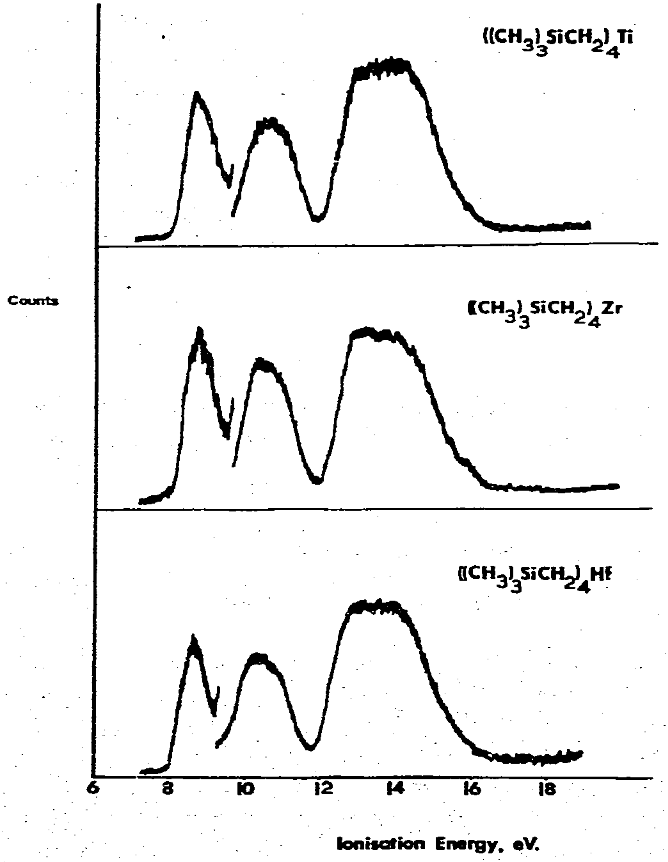


Fig. 1. He(I) PE spectra of $[(CH_3)_3SiCH_2]_4M$; M = Ti, Zr, Hf.

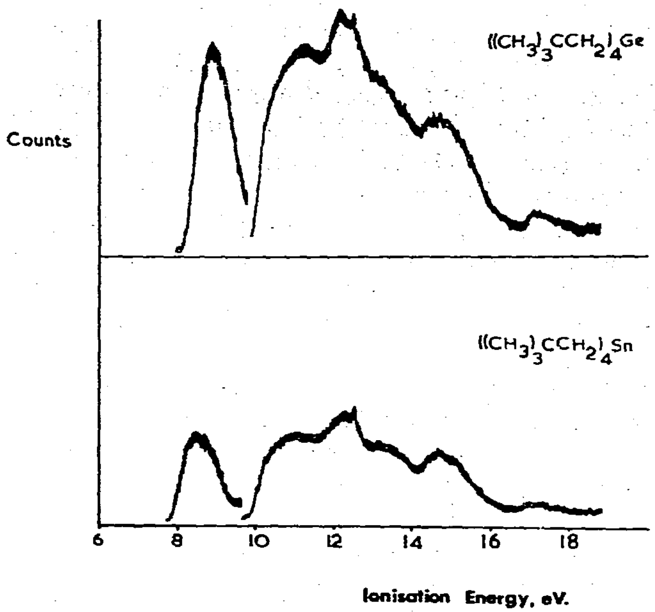


Fig. 2. He(I) PE spectra of $[(CH_3)_3CCH_2]_4M$; M = Ge, Sn.

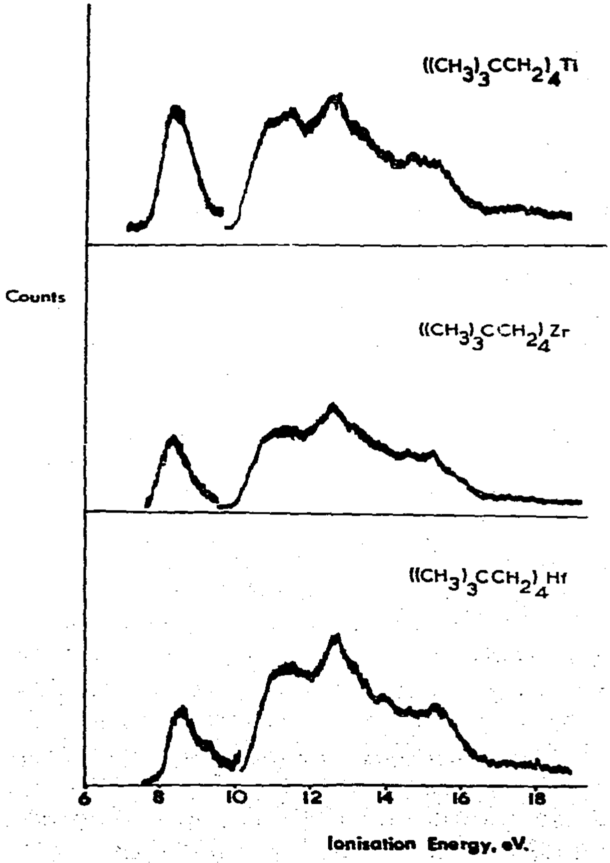


Fig. 3. He(I) PE spectra of $[(CH_3)_3CCH_2]_4M$; M = Ti, Zr, Hf.

Discussion

The spectra are shown in Figures 1 - 3 and the first three vertical ionisation potentials (IP's) are recorded in Tables 2 and 3. The first band in all spectra was recorded on an ordinate scale of 0 - 50 counts per sec, while the remaining bands were recorded on the scale 0 - 150 counts per sec.

The second and third bands in the spectra of the metal alkyls show a general similarity to the overall spectra of the corresponding free ligands, the broadness of the bands being due to mutual interaction of the ligands. The positions of these bands are almost independent of the Group IV central metal atom, indicating that a localised bond model is appropriate for these orbitals.

If the local symmetry around the central metal atom is assumed to be T_d, and infrared and Raman studies support this conclusion (although there probably is some distortion) [12] then the first band in the spectra of the metal alkyls is readily assignable from previous studies [6] to an orbital of symmetry T_2, which is supported by the observed intensities in all cases. The vertical IP's of the (trimethylsilyl)methyl compounds are consistently slightly higher than for the neopentyl compounds in accordance with the higher electron releasing properties of the latter ligand, but it is particularly interesting to note the close similarities of the first IP's for all cases except $Ge[CH_2C(CH_3)_3]_4$. Both the *p* and *d* orbitals of the central metal atom are of the correct symmetry to contribute to the highest occupied MO. For the isoleptic transition metal alkyls, the constancy of the first IP down the series appears to indicate a constancy of central atom parameters down the series (unless trends are selfcancelling) or that the highest occupied molecular orbital has little or no central atom character. If the latter explanation held, then M—C chemical bonding would primarily arise from the M—C orbital of A_1 symmetry (in the tetrahedral group), which is obscured by the ligand bands in our spectra. We favour the former explanation, however. It is well known that the properties of zirconium are very similar to those of hafnium (atomic radius, ionic radius, first IP) (data for Ti are also rather similar) and it is on these properties of the central atom that the first IP of the complexes depends. Thus we expect the first IP's of the Group IVA complexes to be similar.

The same effect is not observed for the isoleptic Group IVB complexes, however, where the first IP decreases with increasing size and decreasing electronegativity of the central atom, as for the Group IVB tetramethyls.

The close position of the three upper PE bands for the transition metal complexes on the one hand and the tin analogues on the other suggests that ground state electronic properties are similar. As these bands also correspond to those in $SnMe_4$ (9.7 and 13.4 eV) [6], we conclude that the M—C bond is broadly similar in character in all these compounds; this is consistent also with vibrational data (vide supra). Hence the marked contrast in thermal stability between, for example, $TiMe_4$ and $SnMe_4$ is reasonably attributed to kinetic rather than thermodynamic effects. In these terms, the much higher activation energy for thermal decomposition of $SnMe_4$ compared with $TiMe_4$ is due to a large difference in the energies of the decomposition transition states ($Ti \ll Sn$) rather than to significant differences in the energies of their ground states.

We would expect by analogy with the Group IVB tetramethyls to observe a splitting of the first band due to Jahn—Teller distortion for the lighter central atoms or spin orbit coupling for the heavier atoms. In fact no splitting was observed for the (trimethylsilyl)methyls, and the only observed effect was a broadening of the first band for tetraneopentylzirconium and a definite shoulder on the tetraneopentylhafnium. To account for this it is necessary to consider the possible causes of the observed splitting. Firstly, a Jahn—Teller distortion would be expected to decrease down a particular series of compounds as the central atom increases in size and crowding is reduced. This is not in accord with the observed spectra and Jahn—Teller distortion must be ruled out. Further, the splitting appears to be larger than the atomic spin—orbit splitting constant for hafnium which indicates that spin—orbit splitting is not the cause. It appears then that the splitting is due to a geometric distortion of the MC_4 framework from T_d to D_{2d}; this causes a splitting of the T_2 orbital into B_2 and E components. Such an explanation accounts for the asymmetry in the zirconium compound and the splitting in the hafnium compound; it is also consistent with the reported vibrational data [12]. It is interesting to note that, although the crystal structures have not been determined for these compounds, they have been reported for both Group IVA and Group IVB tetrabenzyls [18]. For these compounds it is found that while the Group IVB complexes have an essentially tetrahedral MC_4 framework, the Group IVA complexes have a distortion which increases down the series. In the case of the (trimethylsilyl)methyls, it would seem that the PE work supports the vibrational studies in concluding that there is little or no distortion of the $M—C_4$ framework from tetrahedral.

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