He(I) and He(II) Photoelectron Spectra of some Organozinc and Organoaluminium Radicals containing 1,2-Bis(t-butylimino)ethane †

Jaap N. Louwen, Derk J. Stufkens, and Ad Oskam *
Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

---

He(I) and He(II) spectra of the organometallic radicals $AlEt_2(L)^{\cdot}$, $ZnMe(L)^{\cdot}$, and $ZnEt(L)^{\cdot}$ ($L = Bu^tN{=}CH{-}CH{=}NBu^t$) generated in the gas phase have been measured. The observed ionization energies (i.e.s) for $AlEt_2(L)^{\cdot}$ are qualitatively in agreement with results from an MNDO calculation performed for the model radical $AlMe_2(L)^{\cdot}$ ($L = MeN{=}CH{-}CH{=}NMe$). Very low i.e.s for the radical electrons (about 6 eV) are observed. These electrons reside mainly in the ligand π^* orbital. Considerable delocalization of all valence molecular orbitals over the whole molecule is demonstrated. Strong charge donation from the N lone pairs towards the metal is apparent both in the i.e.s of the ligand orbitals without metal interactions and in the low i.e. values for Zn 3*d* ionizations.

In recent years there has been considerable interest in inorganic and organometallic complexes containing 1,4-diazabutadienes (L, $RN{=}CH{-}CH{=}NR$) and related ligands.[1] This type of ligand exhibits a variety of bonding modes as a result of the presence of several frontier orbitals which are of potential use in co-ordination. The presence of both a symmetric and an antisymmetric lone-pair combination at high energy favours σ bonding to both transition and post-transition metals. Butadiene-type π orbitals are also present and the presence of a high-energy π^- orbital, in principle, allows co-ordination to a metal *via* its π system (as postulated in ref. 2). Furthermore, the presence of a low-lying lowest unoccupied molecular orbital (l.u.m.o.) (π^*) of appropriate symmetry allows charge withdrawal with both σ- and π-type co-ordination.

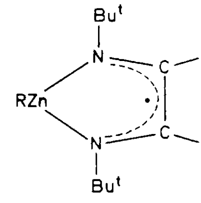
In fact the l.u.m.o. is so low in energy that several non-transition-metal complexes of co-ordinated L [or related molecules such as 2,2′-bipyridine (bipy) and 1,10-phenanthroline] exist in which the ligand is formally negatively charged and has thus become a radical anion.[3-9]

Recently the organometallic radicals $ZnR(L)^{\cdot}$ and $AlR_2(L)^{\cdot}$ ($L = Bu^tN{=}CH{-}CH{=}NBu^t$) have been reported,[10-12] the bipy analogues of which have been reported before and studied extensively by e.s.r. spectroscopy.[5,7]

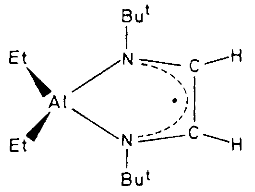
The study of the electronic structure of these compounds is of relevance not only as a contribution to the theoretical study of these unusual organometallic radicals, but also because of the opportunity they present to observe spectroscopically the important π^* orbital of L. An assessment of the energy and character of this orbital is of obvious use in discussing the co-ordination behaviour of ligands L; this energy also relates to the electron affinity of transition-metal co-ordination compounds of L and related ligands. E.s.r. measurements on the reduced complexes of L and bipy with Mo have shown the l.u.m.o. in these compounds to have significant π^* character. The difference in l.u.m.o. participation between L and bipy complexes is caused by the difference in l.u.m.o. energy of these ligands.[13]

Furthermore, a study of the electronic structure of these radicals might be of use in understanding their interesting chemical behaviour, such as the facile C–C coupling and their reactions with alkyl radicals (N-alkylation *vs.* C-alkylation).[1,12]

With this in mind we have undertaken an ultraviolet photoelectron spectroscopic (u.p.s.) study of the organometallic radicals $AlEt_2(L)^{\cdot}$, $ZnMe(L)^{\cdot}$, and $ZnEt(L)^{\cdot}$ ($L = Bu^tN{=}CH{-}CH{=}NBu^t$).



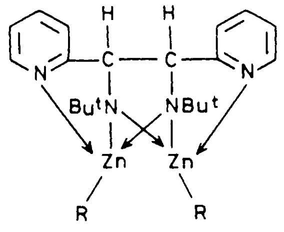
R = Me or Et



Experimental

The spectra were recorded using a Perkin-Elmer PS18 photoelectron spectrometer, equipped with a Helectros Developments hollow-cathode He(I)/He(II) light source. The spectra were calibrated with respect to He, Ar, and Xe as internal references.

The samples used to generate the organozinc radicals were obtained by treating ZnRCl with $K^+L^{\cdot-}$ ($L = Bu^tN{=}CH{-}CH{=}NBu^t$) according to ref. 12. From this reaction a compound is isolated as a white crystalline solid which is also predominantly a dimer in solution according to molecular-weight determinations and n.m.r. data. Solution ^1H and ^{13}C n.m.r. studies indicate that this dimer has a structure similar to that determined by *X*-ray crystallography for compound (1) *i.e.* with C–C coupling (see Results and Discussion section). In the aluminium case the sample used was the yellow-green oil resulting from the reaction between $AlEt_2Cl$ and $K^+L^{\cdot-}$.[12]



(1)

The samples were introduced into the spectrometer by a sample holder which was loaded with the compound in an inert atmosphere (N_2)-box. Attempts to run a spectrum of compound (1) met with failure since heating of the dimer to temperatures of about 100 °C resulted only in decomposition and the spectrum of the free ligand was observed.

---

† *Non-S.I. unit employed*: eV ≈ 1.6 × 10^{-19} J.

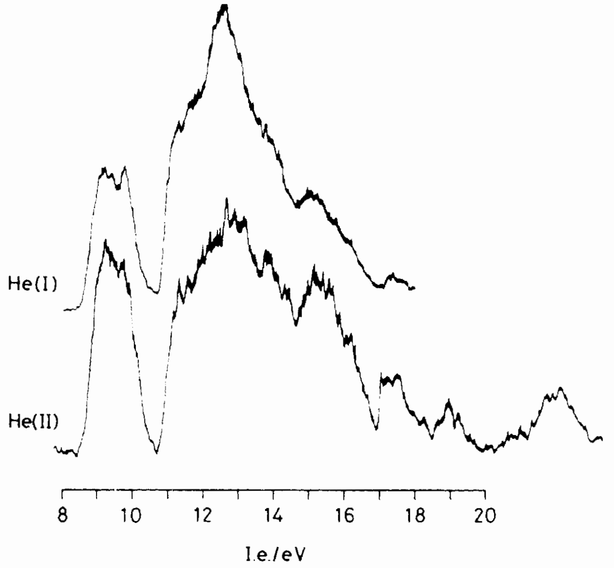


Figure 1. He(I) and He(II) photoelectron spectra of $Bu^tN=CH-CH=NBu^t$

The Electronic Structure of the Compounds.—Prior to assigning the spectra we will review the relevant electronic energy levels in these organometallic radicals of Zn and Al. The free ligand $Bu^tN=CH-CH=NBu^t$ has been studied before by He(I) photoelectron spectroscopy and CNDO m.o. calculations.[14] Its He(I) and He(II) spectra are depicted in Figure 1. The He(I)/He(II) intensity ratio supports the assignment of the broad band at lowest ionization energy (i.e.) to the two N lone-pair combinations n^+ and n^- and of the second band (strongly overlapping with the first) to the π^- orbital. The more significant N-orbital participation in both n_N m.o.s results in a larger He(II) intensity of the first band with respect to the second.

Some care should be taken, however, in comparing the i.e. values for free and co-ordinated $Bu^tN=CH-CH=NBu^t$. In the organometallic radicals it is co-ordinated in a *s-cis* conformation. Because of steric repulsion between the N lone-pair orbitals this structure is highly unfavourable for the free molecule.

A gas-phase diffraction study was performed[15] which showed the molecule $Bu^tN=CH-CH=NBu^t$ to possess a twist angle of only 65°. This is surprising since solid-state crystallography[16] on $C_6H_{11}N=CH-CH=NC_6H_{11}$ and n.m.r. studies on $RN=CH-CH=NR$ molecules co-ordinated in a unidentate manner to a transition-metal atom[17,18] both show the di-imines to be in the planar *s-trans* conformation (with a twist angle of 180°). This structure is in much better agreement with the u.p. spectra.

One important point is that the small difference in i.e. between n_N^+ and n_N^- arises from mutual cancellation of through-bond and through-space interactions. According to Hoffmann's model calculations on 1,4-dehydrobutadienes,[19] this interaction of localized orbitals with three intervening σ bonds is in accord with a planar *s-trans* structure. This geometry is also indicated by the large energy difference between π^+ and π^-.

On this evidence we will assume the u.p. data of $Bu^tN=CH-CH=NBu^t$ to refer to the planar *s-trans* structure in which orbital energies for π orbitals especially will be close to the energies for the corresponding orbitals in the *s-cis* structure because of the similar overlap between localized $\pi(C=N)$ orbitals.

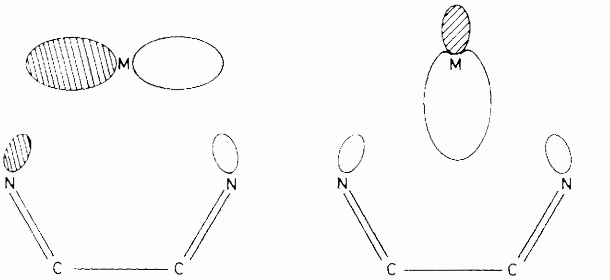


Figure 2. Interaction of metal orbitals with ligand N lone-pair orbitals n_N^- (left) and n_N^+ (right)

Because of its symmetry, the π^- orbital is not suitable for bonding of di-imines to a metal, other than through a δ interaction with a metal *d* orbital. However, on Zn the 3*d* orbitals are fully occupied and chemically inert (see below), while the empty 3*d* orbitals on Al and 4*d* orbitals on Zn are too high in energy and afford little opportunity for donor interaction from the ligand L.

As far as the n^+ and n^- orbitals are concerned we note that their respective roles in non-transition-metal complexes are different from those in transition-metal complexes. In the latter the most favourable σ interaction is donation of charge from an n^- orbital into an empty metal *d* orbital. By contrast, with non-transition metals the dominant σ interaction will be with metal *sp* hybrids. In Figure 2 are depicted the interactions of metal *s* and *p* orbitals with n^- (left) and n^+ (right). From the fact that the metal *s* orbital must participate in the hybrid which mixes with the n^+, while the n^- will mix only with a pure *p* orbital, one expects the n^+-metal interaction to be more favourable because of the different orbital energies of metal *s* and *p* orbitals.[20]

The n^+-metal interaction will also be favoured by the N-M-N bite angle which is less than the typical angle for sp^2 or sp^3 hybridization. *X*-Ray crystallography on compound (1) has shown an N-M-N bite angle of 87°,[12] which may be taken as a first approximation for the angle in the zinc radicals. For the aluminium radical the bite angle is also estimated to be less than 90° (a value of 87° was calculated by MNDO, see below).

The most important orbital of $RN=CH-CH=NR$ relating to this study is of course the π^* orbital. Since it is the bearer of negative charge for these ligands it is worthwhile examining its bonding properties. Because of its symmetry it is, in principle, capable of interaction with orbitals of π symmetry on the post-transition-metal moiety, namely the p_π orbital on the metal and orbitals in which this atomic orbital participates. This M-L interaction thus offers the possibility of some charge delocalization towards the metal and the alkyl groups.

In the zinc complexes one finds, apart from the above, a fully occupied subshell of 3*d* orbitals. It has by now been fairly well established that Zn is essentially a non-transition metal, *i.e.* the 3*d* electrons are chemically inert. In keeping with this core-like character, i.e.s for ionizations from these orbitals are found to be relatively high, around 17 eV for many zinc compounds,[21,22] well within the region of ionizations from $\sigma(C-H)$ and $\sigma(C-C)$ type orbitals. However, the 3*d*-type ionizations can be distinguished by their large He(II) cross-section,[22] contrasting with σ ionizations which are known[23] to have smaller He(II) than He(I) cross-sections. A comparison with data from previous[21] and forthcoming[24] studies on several compounds which can formally be treated as consisting of a Zn^{2+} ion co-ordinated by two univalent negative ions is of interest because the location of the Zn 3*d* levels is only dependent upon the repulsive effect of the co-

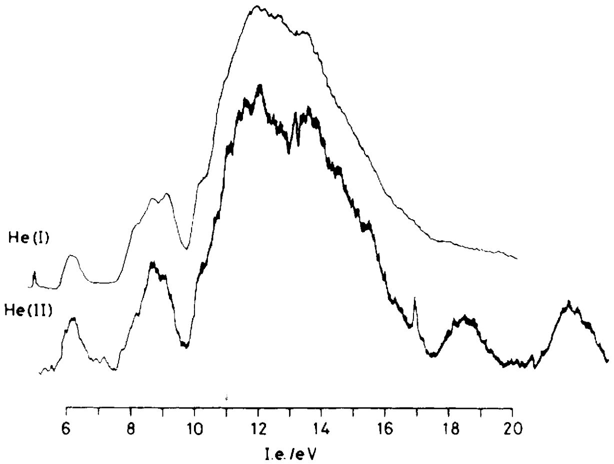


Figure 3. He(I) and He(II) photoelectron spectra of AlEt$_2$(L)$^{\cdot}$ (L = Bu^{t}N=CH–CH=NBu^t). The sharp band at 4.99 eV in the He(I) spectrum of this and the other radicals is due to He

Table 1. Ionization energies (eV) of the compounds (L = Bu^{t}N=CH–CH=NBu^t)

	L	AlEt$_2$(L)$^{\cdot}$	ZnMe(L)$^{\cdot}$	ZnEt(L)$^{\cdot}$
π^*_L		6.14	5.89	5.98
π^-_L	9.78	8.76	8.41	8.42
σ(M–C)		8.33(−) 9.14(+)	8.69	8.42
n^-	9.26	10.3	9.17	9.31
n^+				
d_{Zn}			15.5	15.5

Table 2. Ionization energies for AlMe$_2$(L)$^{\cdot}$ (L = MeN=CH–CH=NMe) as calculated by MNDO (using Koopmans' theorem) compared to the corresponding experimental ionization energies for AlEt$_2$(L)$^{\cdot}$ (L = Bu^{t}N=CH–CH=NBu^t). All values in eV

	AlMe$_2$(L)$^{\cdot}$ (MNDO)	AlEt$_2$(L)$^{\cdot}$ (Exptl.)
π^*_L	4.12	6.14
σ^-(Al–C)	9.60	8.33
π^-_L	10.73	8.76
σ^+(Al–C)	10.61	9.14
n^-_L	12.05	10.3

ordination environment, and hence qualitative data on the relative crystal-field effects of the ligands can be gained.

Furthermore, in the compounds under study, M–C bonds exist. For the zinc complexes we can derive an approximation for the i.e. of a localized Zn–C bonding orbital by taking the mean value of the i.e.s due to the σ_g and σ_u Zn–C orbitals in ZnMe$_2$.[22] Thus we arrive at a value of 10.37 eV, but mixing of the Zn–C orbital with orbitals on the ligand L will change the ionization energy of the resulting m.o.

In the aluminium radical two Al–C orbitals exist but a value for the localized orbital cannot be derived; although the i.e. for the e(Al–C) orbital in AlEt$_3$ (C_{3v} symmetry) has been established as 9.76 eV,[25] a value for the a(Al–C) orbital is lacking.

Results and Discussion

In discussing the spectra, the validity of Koopmans' theorem[26] will be assumed, *i.e.* ionization bands will be identified with canonical molecular orbitals. Apart from the radical electron, all electrons will be assumed to reside in doubly occupied orbitals. In keeping with this, m.o. calculations have been carried out in the restricted Hartree-Fock scheme.

Generation of the Radicals.—It has to be realized that the radicals have not been isolated as such. In the zinc case the sample used was the dimer obtained from the reaction between ZnRCl and K$^+$L$^{\cdot-}$ (L = Bu^{t}N=CH–CH=NBu^t). It is known[12] that in solution this dimer is in equilibrium with the monomer radical with the rate being dependent upon the temperature. The equilibrium is, however, predominantly on the side of the dimer. Since spectra of possible decomposition products (L, ZnR$_2$[22]) are not observed, the spectrum recorded must be due either to the monomer or to the dimer. The very low intensity and i.e. of the band of lowest i.e. supports the assignment of the spectrum to the persistent radical instead of the dimer as the spectrum of the latter would only show bands resulting from doubly occupied orbitals of bonding character.

The oil isolated from the reaction between AlEt$_2$Cl and K$^+$L$^{\cdot-}$ (L = Bu^{t}N=CH–CH=NBu^t) has been shown by e.s.r. and n.m.r. measurements to consist in solution mainly of the persistent radical AlEt$_2$(L)$^{\cdot}$.[12] In this case also, u.p. spectra of possible decomposition products are absent, indicating that the spectrum recorded may likewise be assigned to the radical. The appearance, in the zinc case, of a weak band at very low i.e. comparable to the band that was assigned to ionization of the radical electron supports the assignment of the spectra to the monomeric organometallic radical species in the zinc case.

The Spectrum of AlEt$_2$(L)$^{\cdot}$ (L = Bu^{t}N=CH–CH=NBu^t).—The spectrum (Figure 3 and Table 1) exhibits a small band at 6.14 eV and a strongly overlapping set of three bands between 8 and 10 eV, the first and third of which seem to lose some intensity with respect to the second on going from He(I) to He(II). Between 10 and 17 eV a broad unresolved band, consisting of ionizations from Et and ligand σ orbitals (plus the ligand π^+ orbital) can be observed. To assign this spectrum, MNDO m.o. calculations[27] have been performed on the model radical AlMe$_2$(L)$^{\cdot}$ (L = MeN=CH–CH=NMe). The geometry was fully optimized within the restriction of C_{2v} symmetry with the exception of structure parameters for the CH$_3$ groups which were given standard values.

The i.e.s for AlEt$_2$(L)$^{\cdot}$ are compared in Table 2 with those calculated for the model using Koopmans' theorem.[26] It can be seen that there exists a reasonable qualitative agreement between the measured and the calculated i.e.s that break down into three separate regions. The first (lowest-energy) region possesses one ionization from the orbital occupied by the radical electron. The second region contains three distinct ionizations, while the third region is in both cases almost a continuum of energy levels.

According to the calculations the lowest i.e. of the last group is reasonably well separated by about 0.5 eV from the second band, but the differences between the following bands are all less than 0.3 eV. This theoretical prediction seems to agree with the experimental spectrum which in fact exhibits a small shoulder at 10.3 eV on the broad σ-orbital band.

In view of this qualitative agreement we have confidence in assigning experimental ionization events within the first two regions to a calculated ionization in the corresponding region. The relevant calculated molecular orbitals are depicted in Figure 4 according to the method of Haselbach and Schmelzer.[28]

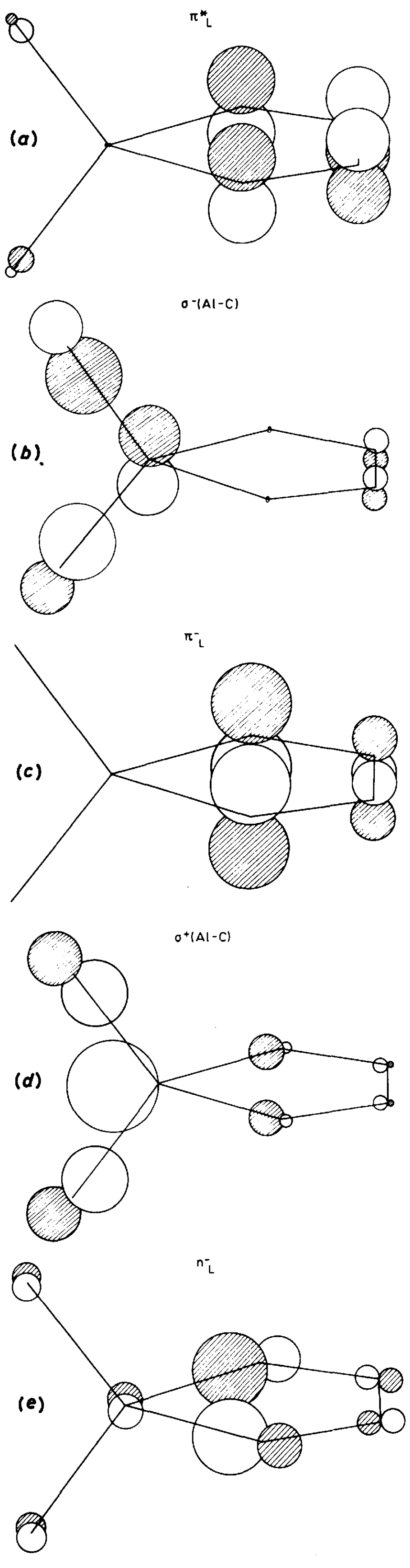


Figure 4. The upper five m.o.s calculated for $AlMe_2(L)^{\cdot}$ (L = MeN=CH–CH=NMe) by MNDO. For details refer to text

The lowest-i.e. band in the spectrum results from ejection of an electron from an orbital which is mainly ligand π^* in character mixed with σ(Al–C) in an antibonding fashion [Figure 4(*a*)]. This character of the orbital in which the radical electron is located agrees well with e.s.r. data on $AlEt_2(L)^{\cdot}$ (L = Bu^tN=CH–CH=NBu^t),[12] where the radical electron was found to be mainly on the ligand but also to a noticeable extent on the ethyl moieties. This is also in agreement with e.s.r. findings on a wide range of organometallic bipy radicals where the radical electron is shown to reside mainly on the ligand. The orbital in which this electron resides is predicted by Hückel m.o. theory to be that analogous to the ligand π^* orbital.[6–8]

The experimental i.e. of 6.14 eV for $AlEt_2(L)^{\cdot}$ shows that the value (4.12 eV) calculated for the model is much too low, especially when the smaller repulsion of methyl substituents *vs.* tertiary butyl substituents is taken into account. Obviously, although the order of magnitude is correct, the MNDO scheme is unable to give a satisfactory orbital energy for this unusual electronic arrangement. Although inclusion of Al 3*d* orbitals into the method might improve the situation somewhat by stabilizing the π^* orbital [Figure 4(*a*)], the basic problem is the prediction of the electron affinity of the ligand part. The l.u.m.o. of MeN=CH–CH=NMe is calculated by MNDO to have an orbital energy close to 0 eV which is unrealistic as it is incompatible with the fact that such compounds are readily converted into a radical anion by metallic lithium, sodium, and potassium.[4]

The following three measured ionization energies agree fairly well with the corresponding group of orbital energies. In increasing i.e. these calculated orbitals are in approximate terms the antisymmetric Al–C [σ^-(Al–C)], the symmetric Al–C [σ^+(Al–C)] and the π^- [Figure 4(*b*)—(*d*)]. In the spectrum the first (lowest i.e., 8.33 eV) and third (highest i.e., 9.14 eV) bands lose intensity with respect to the second (8.76 eV) upon going from He(I) to He(II). On the basis of the well documented cross-sections of atomic orbitals,[23] we assign the first and third bands as σ^-(Al–C) and σ^+(Al–C) respectively and the second as π^-_L. This ordering of the last two bands is at variance with the MNDO calculations.

The closeness in energy of both the actual and the calculated σ(Al–C) orbitals (<1 eV) is due to mixing of σ^- with π^*_L (causing a rise in i.e.) [Figure 4(*b*)] and of σ^+ with n^+_L (causing a lowering in i.e.) [Figure 4(*d*)].

The π^- orbital with a nodal plane passing through Al [Figure 4(*c*)] is a pure ligand orbital due to the unavailability of $AlEt_2$ orbitals of the right symmetry (σ CH orbitals on ethyl and Al 3*d* orbitals excluded). The measured i.e. of the π^-_L is about 1 eV lower than the value in the free ligand (9.78 eV). This is consistent with the MNDO calculations which show that the net charge effect of an extra electron in the π^* orbital and donation towards Al results in a negative charge on the ligand L. The fact that the calculated π^-_L orbital energy is too low is at least partly due to the simplifying approach of using a methyl instead of a more repulsive tertiary butyl substituent at N in the calculations.

From the other orbitals we note that the n^-_L orbital is mixed with an antibonding Al–C orbital of π-symmetry with respect to the C–Al–C plane to provide charge withdrawal from the ligand [Figure 4(*e*)]. On the basis of the MNDO calculations we tentatively assign the shoulder at 10.3 eV to this n^-_L orbital. As predicted earlier, the orbital is found to be more stabilized than the n^-_L orbital on the free ligand L and level interaction with σ^+(Al–C) (see above) will add to this stabilization.

The Spectra of $ZnR(L)^{\cdot}$ (R = Me *or* Et; L = Bu^tN=CH–CH=NBu^t).—As with $AlEt_2(L)^{\cdot}$, the spectra (Figures 5 and 6)

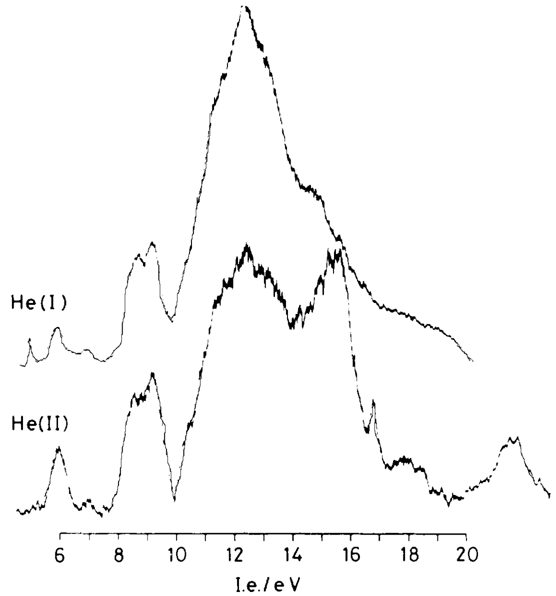


Figure 5. He(I) and He(II) photoelectron spectra of $\mathrm{ZnMe(L)^{\bullet}}$ ($\mathrm{L = Bu^tN{=}CH{-}CH{=}NBu^t}$)

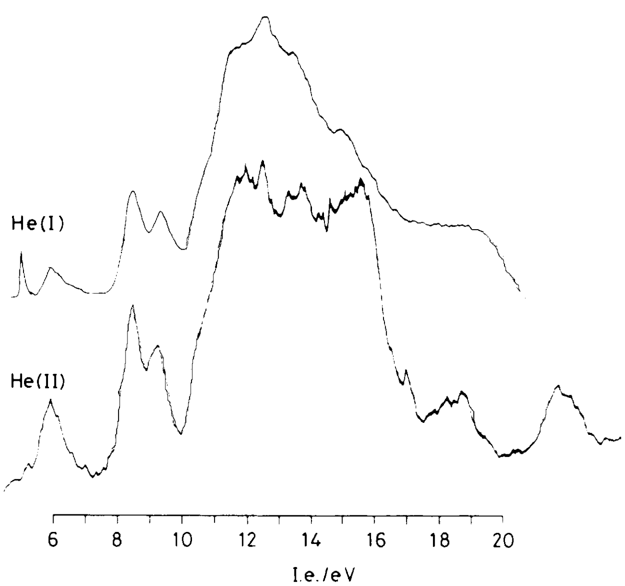


Figure 6. He(I) and He(II) photoelectron spectra of $\mathrm{ZnEt(L)^{\bullet}}$ ($\mathrm{L = Bu^tN{=}CH{-}CH{=}NBu^t}$)

exhibit a small band at very low i.e. Between 8 and 10 eV are three bands. Two of these are coincident (Et) or nearly so (Me), while the third appears more or less separated. From 10 to 17 eV a broad unresolved band can be observed from which in He(II) a maximum of about 15.5 eV arises.

The first small band at low i.e. is again assigned to ionization of an electron from an orbital consisting primarily of the π^*_{L} orbital with some metal and σ(CH) character. This is in agreement with e.s.r. data,[12] which show the electron to reside mainly on the ligand. However, unlike the spectrum of the aluminium compound, this low-i.e. band has an unusual appearance with a quite distinct tail which seems to be due to a very small extra band at about 7 eV. The nature of this band is not clear. Since it appears exclusively in the spectra of the zinc radicals it will be due either to some other product of the reaction that gives rise to the radicals (see above) or to some measure of association between the radicals even in the gas phase at elevated temperature. Therefore it is obvious that only clear band maxima can be discussed in the spectra of the zinc compounds.

The three bands between 8 and 10 eV have in total six times the intensity of the first band in He(I), indicating that three doubly occupied orbitals give rise to ionizations in that region. To assign these ionizations it is first necessary to discuss the relation between the spectra of $\mathrm{AlEt_2(L)^{\bullet}}$ and $\mathrm{ZnEt(L)^{\bullet}}$ ($\mathrm{L = Bu^tN{=}CH{-}CH{=}NBu^t}$). Instead of two Al–C orbitals only one Zn–C orbital is present in the zinc compound and for its i.e. the mean value of the Al–C i.e.s may be taken as a first approximation. If the overall charge on the ligand moiety does not differ too much between the radicals of Zn and Al, and thus the π^- band remains at about the same i.e., the expected σ(Zn–C) band will nearly coincide with the band due to the unaffected π^-_{L} orbital.

In the zinc case the n^-_{L} i.e. will be lower than in the aluminium compound since differences between e.s.r. data for $\mathrm{ZnEt(L)^{\bullet}}$ and $\mathrm{AlEt_2(L)^{\bullet}}$ (L = 2,2′-bipyridine) could be rationalized by postulating that N→M donation with $\mathrm{AlEt_2}$ is stronger than with ZnEt.[7] This results in a more negative charge on N in the zinc than in the aluminium radical. The latter effect will also lead to some decrease in the i.e. value for ionizations from ligand π-type orbitals on going from Al to Zn.

Indeed, the spectrum of $\mathrm{ZnEt(L)^{\bullet}}$ agrees perfectly with the above predictions. The actual coincidence of bands ascribed to π^-_{L} and σ(Zn–C) may seem highly fortuitous, especially since the observed σ(Zn–C) i.e. is far removed from the mean value of σ^+(Zn–C) and σ^-(Zn–C) in $\mathrm{ZnMe_2}$ (10.5 eV [12]), but the assignment can be proven by comparing the spectra of the methyl and ethyl compounds. The band most affected by this substitution is that due to σ(Zn–C), since interaction with σ(C–H) and σ(C–C) orbitals in the R group lowers the σ(Zn–C) i.e. Thus, upon substitution of Me by Et an ionization previously at 8.69 eV now occurs at 8.42 eV while no other bands are destabilized to that extent (see Table 1). Apart from confirming the assignment, this result seems to indicate that there is not much participation of Et or Me group orbitals in the highest orbital containing the radical electron, since the band corresponding to this orbital is changed only little in i.e. upon replacing Me by Et.

The low i.e. value for σ(Zn–C) can be explained by a strong interaction between the localized σ(Zn–C) and n^+_{L} orbitals, lowering the i.e. of the first and raising the i.e. of the latter.

The assignments for the zinc compounds are summarized in Table 1. Again we note that the π^-_{L} i.e. is less than that of the free ligand, indicating that the effect of an extra electron is not fully compensated by charge withdrawal from the N lone pairs. Obviously, strong donation from N to Zn does exist, otherwise the difference in i.e. for the π^- ionizations between free and co-ordinated L moieties would be of the order of a molecular coulomb integral (the electrostatic repulsion energy between two electrons in two different molecular orbitals, *ca.* 5 eV). This strong donation is further indicated by the unusually low i.e. value for the Zn 3*d* ionizations. These occur as a band at about 15.5 eV and are recognized by their high He(II) intensity. Compared to the 3*d* i.e. values for other compounds of Zn in a formal 2+ oxidation state,[21,22,24] this i.e. is very low. Clearly the charge-donating effect of the N lone pairs is felt strongly by the zinc core orbitals.

Conclusions

The u.p. spectra of the organometallic radicals $\mathrm{AlEt_2(L)^{\bullet}}$, $\mathrm{ZnMe(L)^{\bullet}}$, and $\mathrm{ZnEt(L)^{\bullet}}$ ($\mathrm{L = Bu^tN{=}CH{-}CH{=}NBu^t}$) generated in the gas phase can be assigned with the use of information from MNDO calculations, He(I)/He(II) intensity differences, and considerations of orbital character and level interaction. Although bands can to a first approximation be ascribed to orbitals localized on several fragments of the radicals, considerable delocalization exists.

The radical electron resides in an orbital which is mainly of π^* character with some delocalization to the alkyl groups. This is supported by e.s.r. measurements.

Probably due to the extra charge in the ligand π system, there is very strong interaction between the N lone pairs and the metal, leading to unusually low values for the $3d$ i.e.s in the case of the zinc compounds.

Acknowledgements

The authors are greatly indebted to Mr. J. T. B. H. Jastrzebski for preparing the samples and Dr. G. van Koten for critical reading of the manuscript and helpful discussions.

References

1 G. van Koten and K. Vrieze, *Adv. Organomet. Chem.*, 1982, **21**, 151.

2 M. W. Kokkes, D. J. Stufkens, and A. Oskam, *J. Chem. Soc., Chem. Commun.*, 1983, 369; *J. Chem. Soc., Dalton Trans.*, 1984, 1005.

3 H. tom Dieck and K-D. Franz, *Angew. Chem.*, 1975, **87**, 244; *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 249.

4 P. Clopath and A. v. Zelewsky, *Helv. Chim. Acta*, 1972, **52**, 55.

5 J. Boersma, A. Mackor, and J. G. Noltes, *J. Organomet. Chem.*, 1975, **99**, 337.

6 W. Kaim, *Chem. Ber.*, 1981, **114**, 3789.

7 W. Kaim, *J. Organomet. Chem.*, 1981, **215**, 325.

8 W. Kaim, *J. Am. Chem. Soc.*, 1982, **104**, 3833.

9 W. Kaim, *Z. Naturforsch., Teil B*, 1982, **37**, 783.

10 J. T. B. H. Jastrzebski, J. M. Klerks, G. van Koten, and K. Vrieze, *J. Organomet. Chem.*, 1981, **210**, C49.

11 J. M. Klerks, J. T. B. H. Jastrzebski, G. van Koten, and K. Vrieze, *J. Organomet. Chem.*, 1982, **224**, 107.

12 G. van Koten, J. T. B. H. Jastrzebski, and K. Vrieze, *J. Organomet. Chem.*, 1983, **250**, 49.

13 H. tom Dieck, K-D. Franz, and F. Hohmann, *Chem. Ber.*, 1975, **108**, 163.

14 K-D. Franz, Thesis, Johann Wolfgang Goethe University (Frankfurt/Main), 1975.

15 I. Hirgattai and R. Seip, *Acta Chem. Scand., Ser. A*, 1976, **30**, 540.

16 J. J. Keijsper, H. van der Poel, L. H. Polm, G. van Koten, and K. Vrieze, *Polyhedron*, 1983, **2**, 1111.

17 H. van der Poel, G. van Koten, and K. Vrieze, *Inorg. Chem.*, 1980, **19**, 1145.

18 H. van der Poel, G. van Koten, and G. C van Stein, *J. Chem. Soc., Dalton Trans.*, 1981, 2164.

19 R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Am. Chem. Soc.*, 1968, **90**, 1499.

20 C. E. Moore, 'Atomic Energy Levels,' *National Bureau of Standards, Circular* no. 467; 1952, vols. 1 and 2; 1958, vol. 3.

21 J. N. Louwen, R. R. Andréa, D. J. Stufkens, and A. Oskam, *Z. Naturforsch., Teil B*, 1982, **37**, 711.

22 J. S. Tse, G. M. Bancroft, and D. K. Creber, *J. Chem. Phys.*, 1981, **74**, 2097.

23 A. Schweig and W. Thiel, *J. Chem. Phys.*, 1974, **60**, 951.

24 J. N. Louwen, J. T. B. H. Jastrzebski, D. J. Stufkens, and A. Oskam, unpublished work.

25 G. K. Barker, M. F. Lappert, B. Redly, G. J. Sharp, and N. P. C. Westwood, *J. Chem. Soc., Dalton Trans.*, 1975, 1765.

26 T. Koopmans, *Physica (Utrecht)*, 1934, **1**, 104.

27 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899; L. P. Davies, R. M. Guidry, J. R. Williams, M. J. S. Dewar, and H. S. Rzepa, *J. Comput. Chem.*, 1981, **2**, 433.

28 E. Haselbach and A. Schmelzer, *Helv. Chim. Acta*, 1971, **54**, 1299.

Received 4*th January* 1984; *Paper* 4/020