Photoelectron Spectroscopic Investigation of Isomeric Methyl (Isocyanide), η^2-Iminoacyl and η^3-Azaallyl Complexes of Molybdenum and Tungsten†

P. James Daff *,[a] **and Nikolas Kaltsoyannis** *,[b]
[a] *Departamento de Química Inorgánica, Universidad de Sevilla, 41071 Sevilla, Spain*
[b] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK*

Gas-phase ultraviolet photoelectron spectroscopy and extended-Hückel molecular-orbital calculations have been employed to investigate the valence electronic structures of twelve compounds drawn from three general isomeric classes; $[M(Me)(CNR)(CO)_2(\eta^5\text{-}C_5R'_5)]$ [methyl (isocyanide)], $[M\{\eta^2\text{-}C(=NR)Me\}(CO)_2(\eta^5\text{-}C_5R'_5)]$ (iminoacyl) and $[M\{\eta^3\text{-}H_2CC(H)NR\}(CO)(\eta^5\text{-}C_5R'_5)]$ (azaallyl) (M = Mo or W, R = Pr^i or Bu^t, R' = H or Me). Although the methyl (isocyanide) compounds are unstable with respect to isomerisation to the corresponding azaallyls on the time-scale of the photoelectron spectroscopy experiment (*ca.* 4 h), sufficient data were acquired to support the assertion that RNC is a better π donor but poorer π acceptor than CO. The first two bands in the photoelectron spectra of all of the iminoacyl and azaallyl compounds are assigned to the two molecular orbitals containing the four electrons of predominant metal d character. The ionisation energies of these orbitals are *ca.* 0.5 eV lower in the iminoacyl than the azaallyl compounds. The energetic separation of these orbitals is traced to a destabilisation of the 2a' $M(CO)_2(\eta^5\text{-}C_5R'_5)$ fragment orbital *via* a filled–filled interaction with the most stable π orbital of the iminoacyl and azaallyl ligands. The destabilisation is greater in the azaallyl compounds due to the additional involvement of an azaallyl fragment orbital which has been previously termed a 'nitrogen lone pair'. Neither the photoelectron spectroscopic nor the theoretical data are consistent with this description.

Treatment of solutions of $Na[M(CNR)(CO)_2(\eta^5\text{-}C_5R'_5)]$ (M = Mo or W, R = alkyl or aryl, R' = H or Me) in tetrahydrofuran with MeI at low temperatures is known to produce the methyl (isocyanide) derivatives $[M(Me)(CNR)(CO)_2(\eta^5\text{-}C_5R'_5)]$.[1,2] Recent studies have demonstrated that it is possible to isolate pure, crystalline samples of these materials at room temperature by judicious choice of M and R, their kinetic stability being favoured by M = W and when R is sterically demanding.[3–6] Increasing the temperature causes an irreversible migration of the Me group to the isocyanide C atom, accompanied by co-ordination of N to M. This constitutes an example of the ubiquitous insertion reaction, the product being an η^2-iminoacyl. Interestingly, heating solutions of methyl (isocyanide) compounds in non-donor solvents promotes formation of a third isomer, the η^3-azaallyl.[3,5,6] There are few literature reports of mononuclear organometallic azaallyl complexes, which is curious as it has been shown experimentally that the azaallyl is thermodynamically the more stable of the three isomers (iminoacyl complexes of the type described in this study isomerise to the corresponding azaallyls at elevated temperatures).[3,4]

It is rare that the opportunity arises to investigate experimentally the electronic structures of a series of isomeric compounds. This system is particularly attractive because the intramolecular spatial redistributions which constitute the transformations take place at only two metal co-ordination positions. The comparatively well understood $M(CO)_2(\eta^5\text{-}C_5R'_5)$ fragment remains essentially invariant between the three complex types, and as such provides a convenient starting point for a discussion of the bonding.

Photoelectron spectroscopy (PES) is well-established as being one of the most useful experimental techniques for the elucidation of the valence electronic structures of transition-metal compounds. In this paper we report the results of a photoelectron (PE) spectroscopic investigation of twelve compounds taken from the three general classes described above. In addition to the variations in compound type, the effects of altering the cyclopentadienyl ligand from $\eta^5\text{-}C_5H_5$ to $\eta^5\text{-}C_5Me_5$ are explored, together with changing the metal atom from Mo to W.

A series of extended-Hückel molecular-orbital (EHMO) calculations has been performed upon idealised structures from each of the three compound types. The aim of these calculations was to provide a general description of the interactions of the frontier orbitals of the $M(CO)_2(\eta^5\text{-}C_5R'_5)$ fragment with those of (Me)(RNC), $\eta^2\text{-}C(=NR)Me$ and $\eta^3\text{-}H_2CC(H)NR$, and to construct essentially qualitative molecular orbital (MO) schemes as guides to spectral assignment. No attempt has been made to reach conclusions solely on the results of the EHMO calculations and, as such, quantitative discussion of them has been kept to a minimum. It was hoped that a combination of the extensive PES data obtained, the EHMO calculations and comparison with the results from previous studies on related compounds would provide a thorough description of the bonding within the systems under investigation.

Experimental

Complexes **1**, **2**, **5**, **9** and **10** were synthesised according to the published procedure.[5] The remaining compounds were synthesised using analogous methods,[6] details of which will appear in a future paper.[7]

The gas-phase ultraviolet photoelectron spectra were measured in the Inorganic Chemistry Laboratory, Oxford using a PES Laboratories 0078 spectrometer interfaced with an Atari

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† *Supplementary data available* (No. SUP 57086, 7 pp.): tabulated ionisation energies. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: 1 eV = 1.6021×10^{-19} J.

1040 ST microcomputer. Both He-I and -II radiation were used for spectral acquisition. Data were collected by repeated scans and the spectra calibrated with He, Xe and N_2. In spectral plots, the dots represent the data points and the continuous line a weighted smooth to the data.

The molecular-orbital calculations employed a modification of the extended-Hückel method with weighted H_{ij} values.[8] Atomic parameters were taken from previous work.[9,10] Bond lengths and angles were taken from crystal structure data where available, and idealised to provide the highest possible symmetry.

Results and Discussion

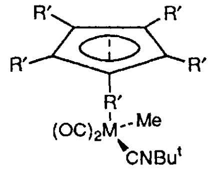
The He I and, where possible, He II PE spectra of [Mo(Me)(CNBu^t)(CO)$_2$(η^5-C_5H_5)] **1**, [Mo(Me)(CNBu^t)(CO)$_2$(η^5-C_5Me_5)] **2**, [W(Me)(CNBu^t)(CO)$_2$(η^5-C_5H_5)] **3**, [W(Me)(CNBu^t)(CO)$_2$(η^5-C_5Me_5)] **4**, [Mo{η^2-C(=NBu^t)Me}(CO)$_2$(η^5-C_5H_5)] **5**, [Mo{η^2-C(=NPr^i)Me}(CO)$_2$(η^5-C_5Me_5)] **6**, [W{η^2-C(=NPr^i)Me}(CO)$_2$(η^5-C_5H_5)] **7**, [W{η^2-C(=NPr^i)Me}(CO)$_2$(η^5-C_5Me_5)] **8**, [Mo{η^3-H_2CC(H)NBu^t}(CO)$_2$(η^5-C_5H_5)] **9**, [Mo{η^3-H_2CC(H)NBu^t}(CO)$_2$(η^5-C_5Me_5)] **10**, [W{η^3-H_2CC(H)NBu^t}(CO)$_2$(η^5-C_5H_5)] **11** and [W{η^3-H_2CC(H)NBu^t}(CO)$_2$(η^5-C_5Me_5)] **12** have been acquired. Tabulated ionisation energies (i.e.s) of the valence bands of all of the compounds bar **2** are available as supplementary material (SUP 57086).

It is not expected that the electronic structure (and consequently PE spectra) of **6, 7** and **8** will be significantly affected by replacement of a Bu^t group on the iminoacyl N by an Pr^i fragment.

The results are presented and discussed according to compound type, beginning with the methyl (isocyanide) species, from which the iminoacyl and azaallyl compounds were prepared.

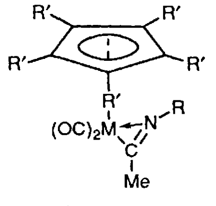
The Methyl (Isocyanide) Complexes.—Complexes **1**–**4** have been shown to exist as a mixture of rapidly interconverting *cis* and *trans* isomers at room temperature in solution,[5,6] and it is reasonable to assume that in the gas phase these species exhibit the same behaviour. The *cis* isomers possess no symmetry elements other than the identity operation, while the *trans* isomers have a mirror plane and therefore C_s symmetry.

A qualitative MO scheme, based upon EHMO calculations of the model complexes *trans*-[M(Me)(HNC)(CO)$_2$(η^5-C_5H_5)] (M = Mo or W) is presented in Fig. 1. The M(CO)$_2$(η^5-C_5H_5) fragment (with *trans* CO groups) possesses C_{2v} local symmetry. The only MOs of this fragment which are expected to be well resolved in the PE spectra of the methyl (isocyanide) complexes are the levels derived from the highest occupied π (e_1) MOs of the cyclopentadienyl ring, and the metal d orbitals (which will, of course, be involved in back-bonding to the empty carbonyl π* MOs). If the M(CO)$_2$ unit is taken to lie in the *yz* plane, the former transform as $b_1 + b_2$, while the d orbitals transform as $2a_1 + a_2 + 2b_1$, as shown in Fig. 1. The carbonyl 5σ and 1π MOs are expected to ionise at comparatively high energies,[11] and therefore will not feature in the spectral region of interest.



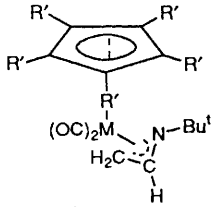
cis, trans
methyl (isocyanide)

	M	R'
1	Mo	H
2	Mo	Me
3	W	H
4	W	Me



η^2-iminoacyl

	M	R	R'
5	Mo	Bu^t	H
6	Mo	Pr^i	Me
7	W	Pr^i	H
8	W	Pr^i	Me



η^3-azaallyl

	M	R'
9	Mo	H
10	Mo	Me
11	W	H
12	W	Me

Introduction of a σ-methyl ligand lowers the symmetry to C_s and brings one more MO into the valence region. The Bu^{t}NC fragment possesses frontier MOs similar to those of a carbonyl ligand, *i.e.* one σ and two π MOs. On electronegativity grounds, all three of these are expected to have lower binding energies than the corresponding MOs of the carbonyl ligands. The complex MOs are filled up to and including the 2a″ level, giving four electrons which are metal d-orbital localised.

PES cannot, of course, probe directly the energies of the unoccupied levels of a compound, but the influences that these levels exert on the energies of filled MOs may be explored. In compounds **1**–**4** it is the stabilisation of the metal d orbitals by back donation into the empty π* MOs of the CO and Bu^{t}NC ligands which is of most interest. A discussion of this is deferred until after a presentation of the PES results.

The He I PE spectrum of **3** is shown in Fig. 2. The spectrum is very similar to that of the closely-related [W(Me)(CO)$_3$(η^5-C_5H_5)],[12] and may be assigned in an analogous manner. Band A is due to ionisation of the four essentially metal d-localised

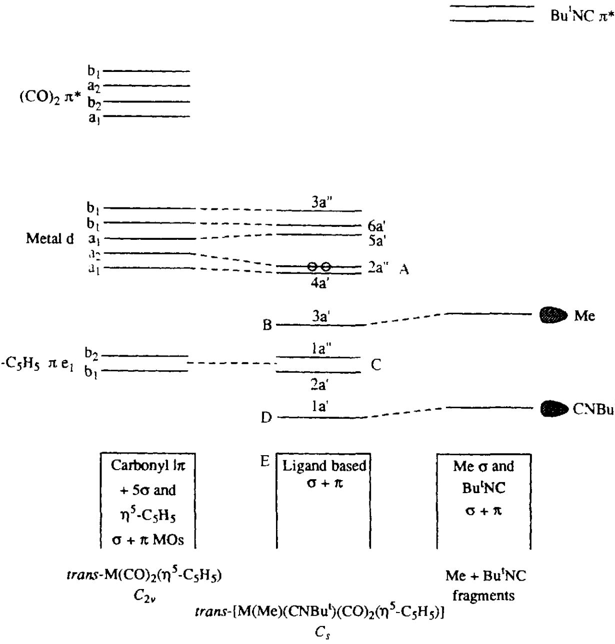


Fig. 1 Qualitative molecular orbital scheme for the methyl (isocyanide) compounds. Upper case letters refer to the corresponding bands in the photoelectron spectra

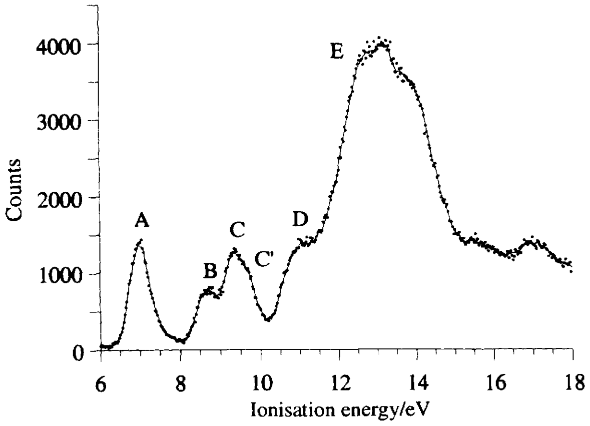


Fig. 2 The He I photoelectron spectrum of [W(Me)(CNBu^t)(CO)$_2$(η^5-C_5H_5)]

electrons. Band B is attributed to the W–Me σ bond (3a′) and band C to ionisation from the MOs derived from the e_1 symmetry orbitals of the cyclopentadienyl ring (2a′ + 1a″). The asymmetry of band C is characteristic of such ionisations, being clearly defined in both $[M(Me)(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) and in $[Mn(CO)_3(\eta^5\text{-}C_5H_5)]$,[13] as well as numerous other complexes containing a cyclopentadienyl–metal fragment. Its origin has been attributed to a Jahn–Teller distortion in the molecular ion,[14] although it has also been suggested that a ground-state distortion of the co-ordinated cyclopentadienyl ring may be the cause.[15]

The main ionisation band, band E, arises from σ MOs of the hydrocarbon ligands, the most stable ring π ionisation, the CO 5σ MOs and the π bonding MOs of Bu^{t}NC. Detailed assignment of this band is not possible, on account of the large number of MOs giving rise to it. Its low i.e. shoulder, band D, may be attributed to the metal–carbon σ bond to the Bu^{t}NC group (1a′). There is also a shoulder to the main ionisation band in $[M(Me)(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) which was assigned to the C–H σ bonds of the methyl group, but it is unlikely that this is the cause of band D, as the i.e. of the band in $[W(Me)(CO)_3(\eta^5\text{-}C_5H_5)]$ is 12.3 eV, compared with 11.0 eV in **3**. The C–H ionisations of the σ-methyl ligand almost certainly lie under the main ionisation band.

The attempted acquisition of the PE spectra of the methyl (isocyanide) complexes was always a somewhat speculative exercise, given their known tendency to isomerise at elevated temperatures (see above). Nevertheless spectra for **1**–**4** were measured, and in all cases the compounds isomerised to the corresponding azaallyl complexes (as evidenced by a change in the form of the PE spectra to that obtained when the azaallyl compounds were measured), although the rate of the transformation differed markedly. Complex **3** gave the initial methyl (isocyanide) spectrum shown in Fig. 2, and it was only after some considerable time (*ca.* 1 h) that the form of the spectrum began to alter. After *ca.* 4 h the spectrum had changed completely to that of **11**. During the intervening period it was possible to follow the progress of the isomerisation by monitoring the growth of the azaallyl signal. At no time was any sign of the iminoacyl compound observed.

This is in agreement with previous studies on these methyl (butyl isocyanide) complexes, in which samples were thermally isomerised in solution.[5,6] The corresponding azaallyls were the only tractable products in the absence of donor solvents. (The effect of donor solvents upon the course of isomerisation has been noted previously,[3,5,6] the observed tendency being for them to promote iminoacyl formation.) That the form of the spectra changed with time indicates that the isomerisation occurs while the compounds are molten in the sample tube rather than in the gas phase. The methyl (isocyanide) and azaallyl species are thus found to have similar sublimation temperatures and rates.

With **1** and **4** a trace of azaallyl signal was present from the beginning of the experiment, although to such a small extent that it proved possible to obtain i.e. data for the methyl (isocyanide) compound. The spectrum of **2**, however, was too contaminated by **10** even at the beginning of the experiment to allow reliable i.e. data to be acquired. Thus the order of decreasing kinetic stability of these methyl (isocyanide) species with respect to transformation into isomeric η^3-azaallyls, as observed in the PE spectrometer, is **3** > **1** ≈ **4** > **2**.

It is informative to compare the i.e.s of **1** and **3** with the corresponding values for $[M(Me)(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W).[12] In both the Mo and W cases, conceptual replacement of a CO ligand by Bu^{t}NC shifts all of the valence bands to lower i.e. This shift is largest for the metal d ionisations (0.83 eV for the Mo compounds and 0.73 eV for the W), and approximately 0.2 eV smaller for the metal–methyl σ bond. The difference in the cyclopentadienyl e_1 i.e. between **3** and $[W(Me)(CO)_3(\eta^5\text{-}C_5H_5)]$ is *ca.* 0.2 eV, but is nearly 0.4 eV for the ionisations of the analogous molybdenum compound.

A PES study of iron tetracarbonyl isocyanide complexes also found a destabilisation of the metal d orbitals on comparison of $Fe(CO)_5$ with $[Fe(CNR)(CO)_4]$ (R = Me, Bu^t, SiMe$_3$ or Ph), and attributed it to a combination of greater filled ligand π orbital/metal d-orbital interaction and reduced metal $\longrightarrow$ ligand π back donation in the isocyanide systems.[16] In MeNC, for example, the filled π MO ionises at 12.46 eV in contrast to a value of 16.91 eV for free CO, suggesting that the isocyanide complexes might be more electron rich at the metal centre. The results presented here support the conclusions reached in that study, *i.e.* that the ionisations which should suffer most from reduced ligand π acceptance (the metal d orbitals) experience a more pronounced destabilisation than the other valence bands.

A comparison of the spectrum of **3** with that of **1** reveals that the metal d-orbital i.e.s vary by only 0.1 eV, with a slightly greater alteration in metal–methyl and cyclopentadienyl e_1 ionisations. The ionisations are at higher i.e. for the tungsten relative to those of the analogous molybdenum compounds. This is also seen to be the case in the methyl (tricarbonyl) compounds. It would appear that there is a stronger interaction between metal and ligand valence orbitals in the W compounds, possibly due to the greater radial extension of the W 5 d orbitals, which results in a stabilisation of the complex MOs with respect to their molybdenum counterparts.

Permethylation of the cyclopentadienyl ring produces the expected changes in the i.e.s of the valence bands, the shift to lower i.e. being greatest for the ring e_1 band and less significant for the W–Me and W d-orbital bands. The effects of ring methylation will be discussed more fully in conjunction with the results obtained on the iminoacyl and azaallyl compounds, whose pentamethylcyclopentadienyl derivatives are not prone to chemical transformations under the conditions of PE spectrum acquisition, in contrast to their methyl (isocyanide) counterparts.

The Iminoacyl and Azaallyl Complexes.—(*i*) *The bent* $M(CO)_2(\eta^5\text{-}C_5R'_5)$ *fragment* (R′ = H *or* Me). A wide range of compounds of general formula $[M(CO)_2L(\eta^5\text{-}C_5R'_5)]$ (R′ = H or Me) exists, in which the CO groups are displaced from the *trans* configuration described earlier, resulting in an overall geometry of the 'three-legged piano stool' type. This work focuses on systems in which L is a three-electron donor η^2-iminoacyl or η^3-azaallyl ligand. The electronic structure of the bent $M(CO)_2(\eta^5\text{-}C_5H_5)$ fragment has been thoroughly treated by previous workers,[17] and is best developed in a coordinate system which places L along the *z* axis, with the *x* axis bisecting the two carbonyls as shown in Fig. 3. There are four orbitals of importance in bonding to L moieties, labelled 1a′ through 3a′ in Fig. 3. The 3a′ orbital is of σ symmetry with respect to the M–L axis, while the 1a′ has a mainly δ interaction with the vacant co-ordination site. The 2a′ and 1a″ orbitals are of π symmetry with respect to the *z* axis, and it is these fragment MOs which will be most significant in bonding to iminoacyl and azaallyl ligands, both of which possess occupied and unoccupied π orbitals.

(*ii*) *The iminoacyl compounds*. The valence MOs of an iminoacyl ligand are qualitatively similar to those of acetylene, *i.e.* the two π and two π* orbitals formed by overlap of the C and N 2p atomic orbitals (AOs) not involved in C–N σ bonding. The bonding π orbitals are more localised on N than C, with the reverse being the case for the π* MOs. Fig. 4 is an MO scheme for the interaction of a bent $M(CO)_2(\eta^5\text{-}C_5H_5)$ fragment with an iminoacyl unit, derived from qualitative considerations and EHMO calculations performed on the model complexes $[M\{\eta^2\text{-}C(=NH)Me\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W). Orbital $\pi_\parallel$ is taken to be the π orbital in the plane of the C–C–N–C skeleton of the iminoacyl ligand, with $\pi_\perp$ lying perpendicular to this plane. There are two limiting conformations which the iminoacyl fragment may adopt. Either it lies in the 'upright' position, *i.e.* in the mirror plane of the $M(CO)_2(\eta^5\text{-}C_5H_5)$ unit, or it bisects this plane. In the MO scheme presented here the iminoacyl ligand is taken to assume the latter geometry, as this

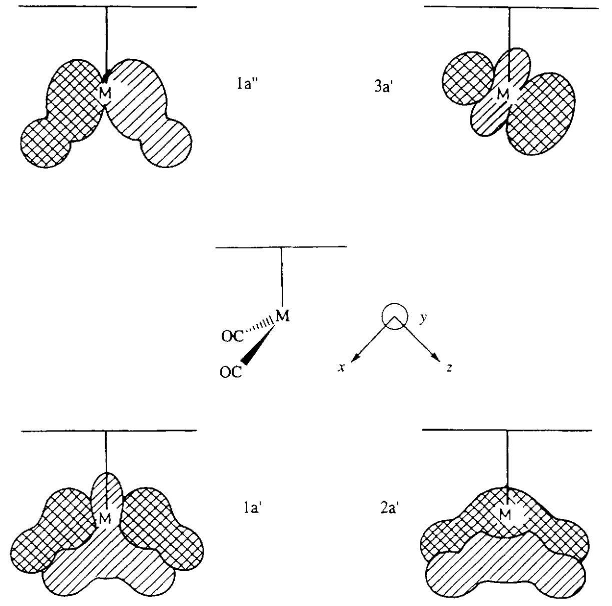


Fig. 3 Schematic contour plots of the 1a′ through 3a′ metal-based valence orbitals of the $M(CO)_2(\eta^5\text{-}C_5H_5)$ fragment. In all cases the plane of the paper is defined as the *xz* plane. The 1a′ (δ), 2a′ (π) and 1a″ (π) orbitals are viewed along the *z* axis (along the vacant co-ordination site). The 3a′ (σ) orbital is viewed in the *xz* plane (perpendicular to the vacant co-ordination site). The cyclopentadienyl ring is represented by a single horizontal line and the carbon and oxygen atoms are unlabelled for clarity

was found to be the case in the crystal structure of $[Mo\{\eta^2\text{-}C(=NPh)Me\}(CO)_2(\eta^5\text{-}C_5H_5)]$,[18] which is the only structurally characterised $[M(CO)_2(\text{iminoacyl})(\eta^5\text{-}C_5H_5)]$ compound. Strictly speaking, of course, this conformation removes the mirror plane from the molecules as the two ends of the iminoacyl fragment are not the same, but the key orbital interactions are not expected to be greatly affected.

The nodal properties of the $\pi_\perp{}^*$ MO of the iminoacyl unit are such that it does not experience a significant interaction with any of the $M(CO)_2(\eta^5\text{-}C_5H_5)$ fragment MOs. The $\pi_\parallel{}^*$ orbital, however, is well set up to receive electron density from the 1a″ donor orbital on the $M(CO)_2(\eta^5\text{-}C_5H_5)$ fragment, an interaction which produces a significant stabilisation of the 1a″ MO. The predominantly δ symmetry of the 1a′ $M(CO)_2(\eta^5\text{-}C_5H_5)$ fragment MO causes it to experience little mixing with the π symmetry iminoacyl valence orbitals, although the 2a′ MO has an interaction with the $\pi_\perp$ iminoacyl MO. The resultant destabilisation of the 2a′ MO is therefore expected to cause a splitting of the single PE band arising from ionisation of the four metal d-based electrons, seen in the spectra of **1**, **3** and **4**. A similar effect has been observed in the spectrum of $[Mn(C_2Et_2)(CO)_2(\eta^5\text{-}C_5Me_5)]$.[19] Fig. 5 presents the He-I and -II PE spectra of **5**, which show five bands below an i.e. of *ca.* 11.5 eV. Above this value comes the broad band associated with the ligand σ ionisations together with the most stable cyclopentadienyl ring π ionisation and the 5σ CO ionisations. As expected, there are two peaks in the region 5.5–7.5 eV, corresponding to ionisation of the four metal d-based electrons. The 0.56 eV splitting of these bands illustrates the destabilisation of the 2a′ $Mo(CO)_2(\eta^5\text{-}C_5H_5)$ fragment MO *via* the aforementioned interaction with the $\pi_\perp$ iminoacyl MO. In support of this, the EHMO calculation on $[Mo\{\eta^2\text{-}C(=NH)Me\}(CO)_2(\eta^5\text{-}C_5H_5)]$ finds a 13% contribution to the complex HOMO from the iminoacyl $\pi_\perp$ MO. The lower maximum and greater half-width of band A with respect to band B may reflect the $Mo(CO)_2(\eta^5\text{-}C_5H_5)/\eta^2\text{-}C(=NBu^t)Me$ antibonding nature of the HOMO.

Band D is characteristic in both profile and i.e. of the highest occupied π (e_1) MO ionisations of the cyclopentadienyl ring.

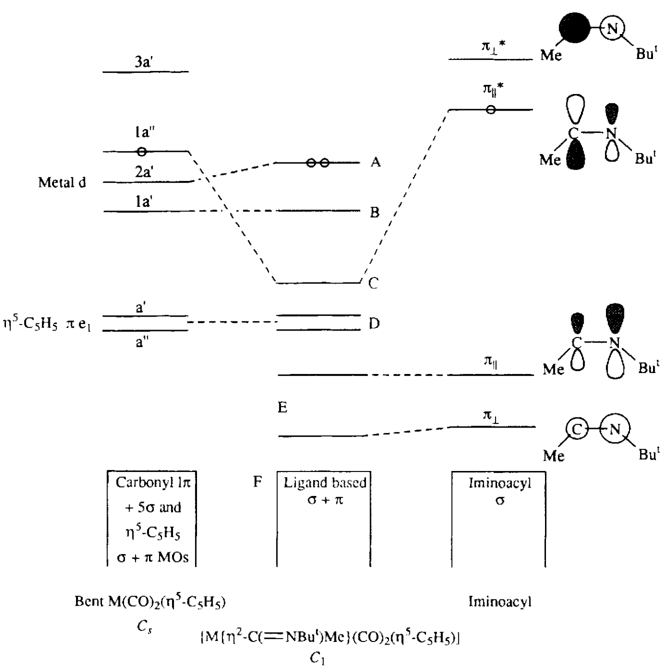


Fig. 4 Qualitative molecular orbital scheme for the iminoacyl compounds. Upper case letters refer to the corresponding bands in the photoelectron spectra of the cyclopentadienyl containing compounds. Relative C and N 2p atomic orbital contributions to the π molecular orbitals of the iminoacyl fragment are represented by lobe/circle sizes and shadings

The band at 8.40 eV (band C) is assigned to the MO which arises from interaction between the 1a″ $Mo(CO)_2(\eta^5\text{-}C_5H_5)$ fragment orbital and the $\pi_\parallel{}^*$ iminoacyl MO. The corresponding band in the PE spectrum of $[Mn(C_2Et_2)(CO)_2(\eta^5\text{-}C_5Me_5)]$, arising from ionisation of the MO formed between the $Mn(CO)_2(\eta^5\text{-}C_5Me_5)$ 1a″ orbital and the alkyne $\pi_\parallel{}^*$ level, was found to be coincident with the MO derived from the $Mn(CO)_2(\eta^5\text{-}C_5Me_5)$ 1a′ fragment orbital.[19] This gave rise to a 1:2 intensity ratio for the first two PE bands, corresponding to ionisation of the six metal d-based electrons. In **5**, however, the greater electronegativity of the N atom results in a closer energy match of 1a″ and $\pi_\parallel{}^*$ orbitals, giving an increased stabilisation and greater ligand character to the resulting complex MO.

Band E is assigned to the filled π orbitals of the iminoacyl ligand. The relative area of this band suggests that it arises from ionisation of four electrons.

The He II spectrum is little different from that acquired with He I radiation. Band A appears to gain in intensity relative to band B, but this is almost certainly due to the increased background in the low i.e. region, arising from the He II β 'shadow' of the main ionisation band, which is observed at an i.e. *ca.* 8 eV lower than the He II α value. All of the bands A–E increase in intensity relative to the main band, but the effect is not great. Other than the metal and H, all of the atoms in the molecule are first-row main group elements, and their valence AOs are predominantly 2p. These do not possess radial nodes in their wavefunction and consequently do not display Cooper minima[20,21] in their photoionisation cross section. As a consequence He I/He II intensity changes are less dramatic than those in molecules containing heavier p-block elements such as Si, P, S and the halogens (except F). It may be that the carbonyl ligand contribution to the highest lying MOs prevents there being a significant increase in the relative intensities of bands A and B with respect to the other valence ionisations, as would be expected were the complex HOMO and NHOMO purely metal d based.

The spectrum of **7** is extremely similar to that of **5**. Most of

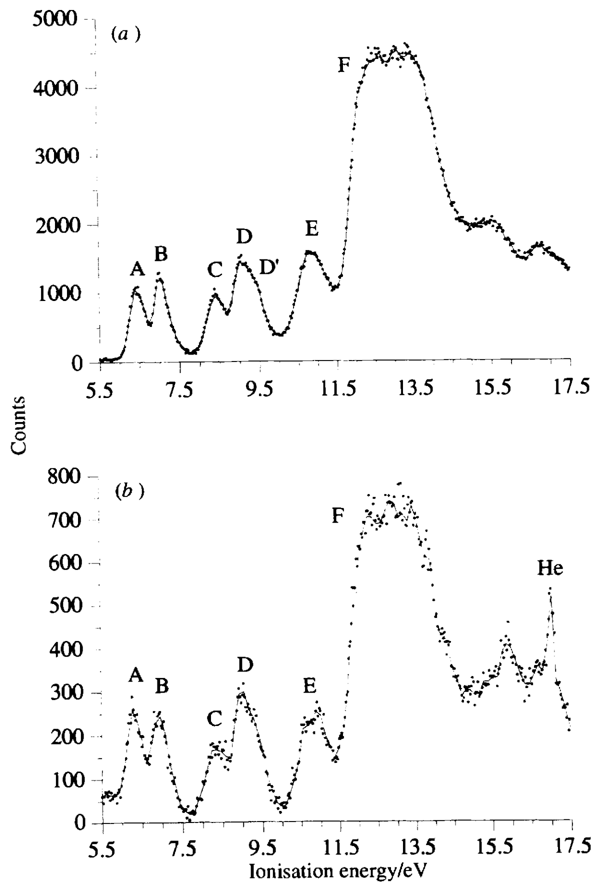


Fig. 5 The He I (*a*) and He II (*b*) photoelectron spectra of [Mo-{η^2-C(=NBu^t)Me}(CO)$_2$(η^5-C$_5$H$_5$)]

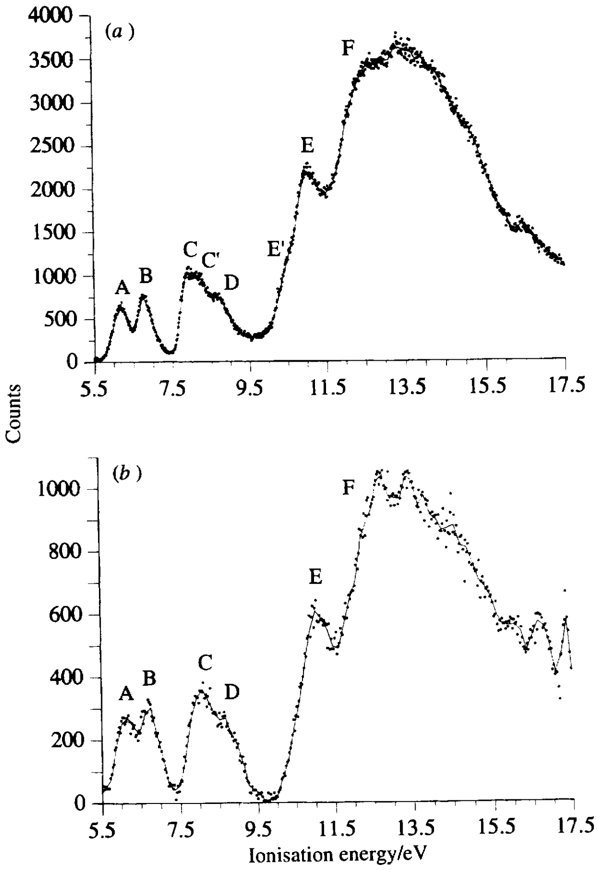


Fig. 6 The He I (*a*) and He II (*b*) photoelectron spectra of [Mo-{η^2-C(=NPr^i)Me}(CO)$_2$(η^5-C$_5$Me$_5$)]

the bands have an i.e. which is between 0.1 and 0.2 eV greater than in the Mo case, as was noted in the methyl (isocyanide) complexes discussed earlier. A more significant effect arises from replacement of the cyclopentadienyl ligand with pentamethylcyclopentadienyl. The He-I and -II spectra of **6** are presented in Fig. 6, and are rather different from the η^5-C$_5$H$_5$ analogue. Bands A and B may still be clearly distinguished and are assigned as in the η^5-C$_5$H$_5$ case. These metal-based ionisations have shifted by *ca.* 0.25 eV to lower i.e. as a result of the inductive effect of the methyl groups on the η^5-C$_5$Me$_5$ rings. The greatest effect of ring methylation, however, is expected to occur in the PE band corresponding to ionisation of the highest occupied e$_1$ η^5-C$_5$Me$_5$ π orbitals, and a comparison of Figs. 5 and 6 reveals distinct changes in the form of the spectrum over the i.e. range 7.5–9.5 eV. The e$_1$ η^5-C$_5$H$_5$ peak, with its characteristically sharp leading edge and high i.e. shoulder, has moved to a substantially lower i.e. in the η^5-C$_5$Me$_5$ compound, such that it lies to lower i.e. than the Mo(CO)$_2$(η^5-C$_5$Me$_5$) $\longrightarrow$ iminoacyl $\pi_{\parallel}$* back-bonding MO. The magnitude of this i.e. shift, 1.15 eV is in excellent agreement with the results of previous studies. The difference in i.e. of the e$_1$ η^5-C$_5$R'$_5$ band between [M(CO)$_3$(η^5-C$_5$H$_5$)] and [M(CO)$_3$(η^5-C$_5$Me$_5$)] (M = Mn or Re) is 1.19 eV for the manganese compound and 1.08 eV for M = Re.[13,14]

The assignment of bands C and C' to the e$_1$ η^5-C$_5$Me$_5$ MOs implies that the complex MO formed by interaction of the 1a'' [Mo(CO)$_2$(η^5-C$_5$Me$_5$)] and $\pi_{\parallel}$* iminoacyl fragment orbitals has shifted 0.34 eV to *higher* i.e. on ring permethylation. One possible explanation for this observation is that the destabilising inductive effect of the η^5-C$_5$Me$_5$ ring on the valence orbitals of the Mo(CO)$_2$(η^5-C$_5$Me$_5$) fragment brings the 1a'' level into closer energetic proximity with the iminoacyl $\pi_{\parallel}$*, producing a greater stabilisation of the resulting complex MO.

Above an i.e. of 9.5 eV the spectrum of **6** is again different to that of **5**. The main band is broader in the η^5-C$_5$Me$_5$ case, and a new band has appeared, at 11.05 eV, with a low i.e. shoulder (E') suggestive of more than one ionisation process. This separation of a band from the low i.e. side of the main ligand σ/low-lying π band as η^5-C$_5$H$_5$ is changed to η^5-C$_5$Me$_5$ has been observed on many previous occasions, and is attributed to ionisations from the ring methyl groups. Interaction between an e symmetry combination of the ring methyl C–H σ bonds and the highest occupied π level of the η^5-C$_5$Me$_5$ ring has been proposed as the cause of the large i.e. shift of the latter between η^5-C$_5$H$_5$ and η^5-C$_5$Me$_5$ complexes,[15] rather than a purely inductive effect. Supporting evidence for this came from a combined X-ray and UV-PES study of [M(CO)$_3$(η^5-C$_5$R'$_5$)] (M = Mn or Re, R' = H or Me), in which the shifts in binding energy of the η^5-C$_5$Me$_5$ C 1 s AOs were found to be only *ca.* one quarter that of the e$_1$ valence band. In the absence of any core binding energy data we can only note that the effects of ring methylation upon the valence PE spectra of our target molecules are entirely consistent with data acquired in previous studies.

It is probable that the low i.e. shoulder to the methyl group ionisations (band E') corresponds to ionisation from the filled π orbitals of the iminoacyl ligand. While these were clearly visible in the η^5-C$_5$H$_5$ case, they are partially occluded by the ring methyl group band in the η^5-C$_5$Me$_5$ containing molecules.

In accord with the observations made when discussing the η^5-C$_5$H$_5$ containing compounds, the spectrum of **8** is very similar to its molybdenum analogue. As before, equivalent complex MOs ionise typically between 0.1 and 0.2 eV to higher i.e. in the tungsten system, reinforcing the observations made when discussing the methyl (isocyanide) spectra.

(*iii*) *The azaallyl complexes.* The azaallyl radical possesses three π valence MOs, analogous to those of the allyl molecule, formed by combination of the N and C 2p functions which lie perpendicular to the N–C–C plane. In addition, the azaallyl group possesses an MO which has been formulated as a N-based lone pair orbital.[5,22] The interaction of the azaallyl moiety with the bent $M(CO)_2(\eta^5-C_5H_5)$ fragment is illustrated in Fig. 7, which was constructed with the aid of EHMO calculations on the model complexes $[M\{\eta^3-H_2CC(H)NH\}(CO)_2(\eta^5-C_5H_5)]$ (M = Mo or W). The lone-pair MO is calculated to lie at an energy midway between the π_1 and π_2 orbitals.

The crystal structure of **9** has been determined,[5] and the azaallyl fragment was found to adopt the *endo* configuration with respect to the $Mo(CO)_2(\eta^5-C_5H_5)$ unit. In this geometry the π_1 MO interacts with the 2a′ $Mo(CO)_2(\eta^5-C_5H_5)$ orbital in a manner similar to that of the iminoacyl $\pi_\perp$, while the π_2 MO possesses the correct nodal properties to interact with the 1a″ $Mo(CO)_2(\eta^5-C_5H_5)$ orbital. Thus many of the features of the iminoacyl MO scheme are present in their azaallyl counterparts. Fig. 8 presents the He-I and -II spectra of **9**.

As for the iminoacyl compounds discussed earlier, the first two bands are assigned to ionisation of the four mainly metal d-based electrons. Band C is assigned to the complex MO derived from interaction between the 1a″ $Mo(CO)_2(\eta^5-C_5H_5)$ π orbital and the π_2 MO of the azaallyl ligand. The π_2 MO of the allyl ligand has been shown to ionise at 9.16 eV in $[Mn(\eta^3-C_3H_5)(CO)_4]$ and at 8.0 eV in $[Nb(\eta^3-C_3H_5)(\eta^5-C_5H_5)_2]$.[14] As noted in ref. 14, the π_2 orbital is expected to mix strongly with the metal d orbitals, the degree of mixing being very sensitive to the energy of the d orbitals in the metal fragment. Consequently the energy of the π_2-derived complex MO may vary significantly between compounds.

It is of interest to compare the i.e.s of bands A–C in the spectra of **5** and **9**. The metal d-based electrons have i.e.s 0.4–0.5 eV lower in the iminoacyl compound, yet the complex MO derived from the $Mo(CO)_2(\eta^5-C_5H_5)$ 1a″ fragment orbital (interacting with $\pi_\parallel{}^*$ in the iminoacyl molecule and π_2 in the azaallyl) is more stable (8.40 *versus* 8.30 eV) in **5** than **9**. The EHMO calculations on these systems indicate that, in relation to the $Mo(CO)_2(\eta^5-C_5H_5)$ 1a″ orbital, the $\pi_\parallel{}^*$ MO of the iminoacyl fragment is 0.5 eV *less* stable while the π_2 azaallyl orbital is *more* stable by 1.25 eV. Thus greater mixing of the 1a″ with $\pi_\parallel{}^*$ is expected in the iminoacyl compound, resulting in an increased stabilisation of the complex MO with respect to the equivalent interaction in the azaallyl complex. The MO giving rise to band C in the spectrum of **9** is therefore expected to resemble the π_2 azaallyl fragment orbital to a greater extent than that in **5** resembles the $\pi_\parallel{}^*$ iminoacyl MO. The relative energies of ligand and metal valence MOs accounts for the greater electron richness of the iminoacyl complex. The fact that the azaallyl π_2 orbital is significantly more stable than the $Mo(CO)_2(\eta^5-C_5H_5)$ 1a″ orbital causes a greater charge shift from metal fragment $\longrightarrow$ nitrogen-containing ligand in the azaallyl molecule, resulting in higher binding energies for the remaining metal d-based electrons.

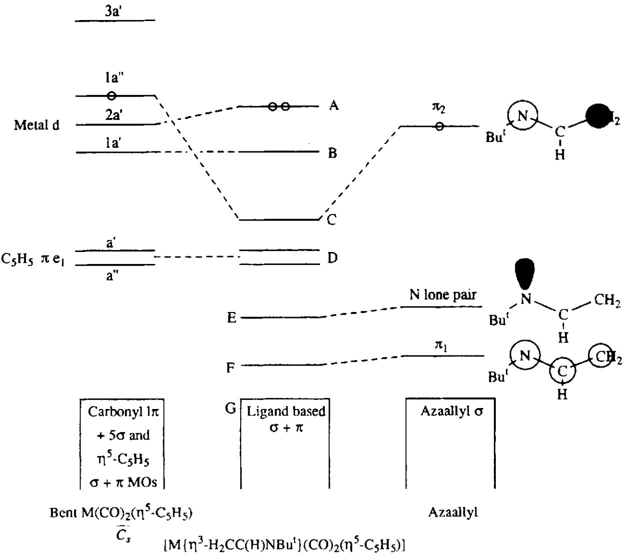


Fig. 7 Qualitative molecular orbital scheme for the azaallyl compounds. Upper case letters refer to the corresponding bands in the photoelectron spectra of the cyclopentadienyl-containing compounds. Relative C and N 2p atomic orbital contributions to the valence molecular orbitals of the azaallyl fragment are represented by lobe/circle sizes and shadings

Bands D and E are almost coincident in the spectrum but, as is clearly illustrated by the $\eta^5-C_5Me_5$ analogue discussed below, there are two distinct ionisations occurring in this region. Band D is assigned to the highest π ionisations of the cyclopentadienyl ring and band E to the N-based lone pair MO of the azaallyl ligand which lies between π_1 and π_2 in the fragment MO scheme.

The main band, characteristic of all of the $\eta^5-C_5H_5$ compounds described in this study, is found above an i.e. of *ca.* 12 eV. It has a low i.e. component (band F) which is not clearly resolved into a distinct peak as is the case in the iminoacyl analogue. This is assigned to the π_1 MO of the azaallyl ligand.

As observed for the iminoacyl compounds, the He II spectrum is little different from the He I. The spectra of the analogous tungsten compounds are also extremely similar to those presented in Fig. 8. Permethylating the cyclopentadienyl ring, however, once again produces a distinct change in the form of the spectrum, illustrated by the He I spectrum of **10** in Fig. 9. It can be seen that the highest $\eta^5-C_5Me_5$ ring π band has shifted relative to the other peaks so that it now overlaps with band C, the π_2/1a″ ionisation.

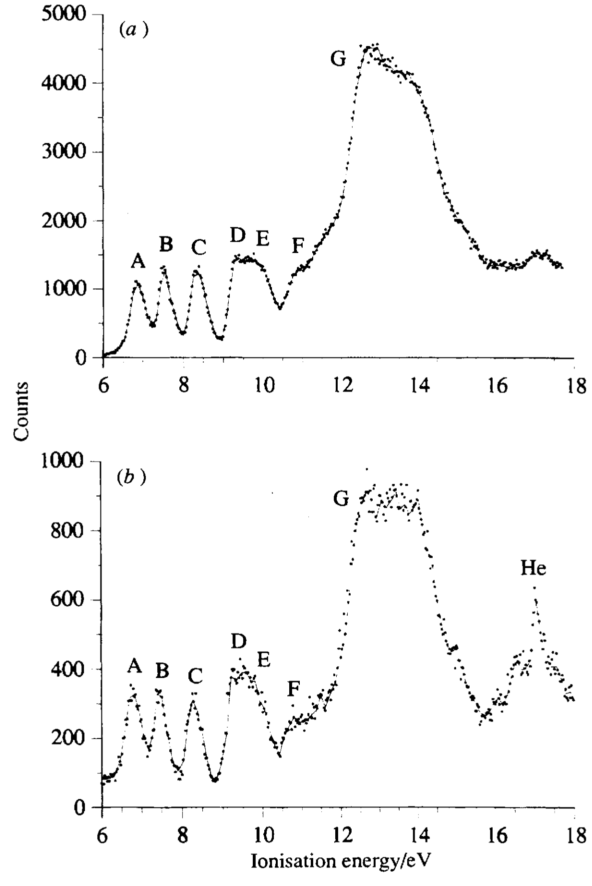


Fig. 8 The He I (*a*) and He II (*b*) photoelectron spectra of $[Mo\{\eta^3-H_2CC(H)NBu^t\}(CO)_2(\eta^5-C_5H_5)]$

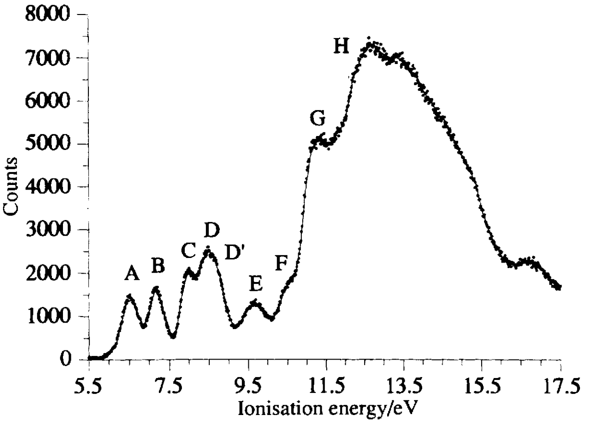


Fig. 9 The He I photoelectron spectrum of [Mo{η^3-$H_2CC(H)$-NBu^t}$(CO)_2$(η^5-C_5Me_5)]

The assignment of bands C and D in **10** is the same as in **9**, in contrast to the iminoacyl compounds for which the 1a″/$\pi_{\parallel}$* band was seen to move to the higher i.e. side of the η^5-C_5H_5 e_1 band on permethylation. The relative areas of bands C and D in the spectrum of **10**, however, make it extremely difficult to invoke an equivalent assignment.

The relative energies of the iminoacyl $\pi_{\parallel}$* and azaallyl π_2 orbitals is again highlighted. Ring permethylation in the iminoacyl series tends to bring the 1a″ and $\pi_{\parallel}$* orbitals into closer energetic proximity, producing greater interaction (as mentioned in comparing **5** and **6**), whereas permethylation of **9** (to produce **10**) increases the energy separation of 1a″ and π_2. The effect is that the interaction of 1a″ and π_2 is reduced, and band C moves to lower i.e.

Band E is much more clearly defined in the spectrum of the η^5-C_5Me_5 complex, and has a similar i.e. to that in the η^5-C_5H_5 compound. The π_1 MO is again found as a shoulder to the main band, which has the characteristic profile of a η^5-C_5Me_5 containing molecule. Complexes **9** and **10** provide an elegant illustration of how modification of one of the ligands in a complex may reveal ionisations that were not previously resolved, by selectively shifting one or more peaks in the PE spectrum.

In all cases, the splitting of bands A and B is greater in the azaallyl compounds than in the equivalent iminoacyl complexes (by *ca.* 0.1 eV). As discussed above, for the iminoacyl compounds this splitting arises from a destabilisation of the 2a′ $M(CO)_2$(η^5-C_5H_5) fragment MO *via* interaction with the $\pi_{\perp}$ orbital of the iminoacyl ligand. What, then, is the nature of the equivalent interaction in the azaallyl complexes? The EHMO calculation on [Mo{η^3-$CH_2C(H)NH$}$(CO)_2$(η^5-C_5H_5)] finds a 5% contribution of the azaallyl π_1 orbital to the complex HOMO, appreciably less than the 13% $\pi_{\perp}$ content of the corresponding MO of [Mo{η^2-C(=NH)Me}$(CO)_2$(η^5-C_5H_5)]. However, a 7% contribution from the N lone pair MO is also predicted in the HOMO, suggesting that the destabilisation of the $Mo(CO)_2$(η^5-C_5H_5) 2a′ MO arises from a filled–filled interaction between the 2a′ level and a combination of π_1 and N lone-pair ligand orbitals in the azaallyl compounds, which together produce a greater effect than the $\pi_{\perp}$ orbital of the iminoacyl ligand.

It has been shown that azaallyl complexes of the type described in this study protonate at the N atom,[22] and this has led to the assertion of the existence of a formal N lone pair. However, the [Mo{η^3-$CH_2C(H)NH$}$(CO)_2$(η^5-C_5H_5)] complex MO derived primarily from this N 'lone pair' is calculated to be only 50% N in character, with approximately 10% contributions from the azaallyl carbon atoms and a similar Mo and H (bonded to N) content. Band E in the PE spectrum of **10** (Fig. 9), which is assigned to this level, is quite broad, in contrast to the sharp features usually associated with lone-pair ionisations. This broadening may well reflect some involvement of the ligand MO with the $Mo(CO)_2$(η^5-C_5Me_5) 2a′ level. Thus the PES and EHMO results are in agreement in suggesting that it is not strictly correct to refer to this orbital as a lone-pair MO, although it is recognised that such a description provides a convenient rationalisation of the protonation site.

Conclusion

The valence electronic structures of twelve compounds drawn from three general isomeric classes [(methyl (isocyanide), iminoacyl and azaallyl] have been studied using gas-phase PES supported by EHMO calculations. The methyl (isocyanide) complexes proved to be unstable with respect to isomerisation to the corresponding azaallyls. Nonetheless, sufficient reliable i.e. data were obtained to permit comparison of [M(Me)(C-NBu^t)$(CO)_2$(η^5-C_5H_5)] with [M(Me)$(CO)_3$(η^5-C_5H_5)] (M = Mo or W). On conceptual replacement of CO by Bu^tNC, a destabilisation of the MOs of predominant metal d orbital character was observed. This is in agreement with the assertion that RNC is a better π donor but poorer π acceptor than CO.

The band of lowest i.e. in the spectra of the methyl (isocyanide) complexes is assigned to the four metal d-based electrons. In the spectra of the iminoacyl and azaallyl compounds, however, these four electrons ionise as two distinct bands of approximately equal intensity. This energetic separation of the two metal-based complex MOs has been traced to a filled–filled interaction between the 2a′ $M(CO)_2$(η^5-$C_5R'_5$) (R′ = H or Me) fragment orbital and the most stable π orbital of the iminoacyl and azaallyl ligands. The separation of the bands is slightly greater in the azaallyl spectra than in the iminoacyl, possibly on account of the partial involvement in the filled–filled interaction of a ligand orbital which has been previously formulated as a N-based 'lone pair'. Support for this interpretation is found in both the PE spectra and the extended-Hückel calculations.

The iminoacyl compounds are more electron rich at the metal centre than the azaallyl, as judged by the i.e.s of the two metal d-based MOs.

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