Gas-phase Ultraviolet Photoelectron Spectra of $[\{Ni(\eta-C_5H_5)\}_2(\mu-C_2R_2)]$ ($R=H$ or CF_3) Complexes †

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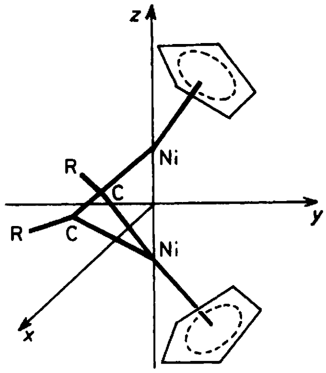
The u.v. photoelectron (p.e.) spectra of $[\{Ni(\eta-C_5H_5)\}_2(\mu-C_2H_2)]$ and $[\{Ni(\eta-C_5H_5)\}_2\{\mu-C_2(CF_3)_2\}]$ are reported. For the first time p.e. spectral features which are related to ionizations from molecular orbitals involved in metal–alkyne back-donation have been detected. The analysis of p.e. results for the CF_3 derivative allow us to discuss in detail the mechanism of interaction between an alkyne and two metallic centres.

During the past few years much attention has been devoted to polynuclear organometallic molecules. They are particularly attractive from a theoretical point of view since they offer a very large variety of bonding situations whose nature is still open to discussion.[1]

Gas-phase u.v. photolectron (p.e.) spectroscopy can make important contributions to our understanding of these systems since it provides a direct measurement of one-electron molecular levels, once Koopmans' theorem is adopted.

Recently, we have focused our attention on the study of the bonding of unsaturated organic substrates with two or more metallic centres.[2–6] The ultimate aim of these studies is the comprehension of the nature of the multicentred metal–ligand interactions which are thought to be similar to interactions between organic molecules and metal surfaces. In the present paper we report the results of a p.e. investigation on $[\{Ni(\eta-C_5H_5)\}_2(\mu-C_2R_2)]$ [$R = H$ (1) or CF_3 (2)].



The p.e. data are discussed qualitatively in terms of symmetry and overlap arguments and by reference to previous results (p.e. and ΔSCF *ab initio* calculations) on the isoelectronic complex $[\{Co(CO)_3\}_2(\mu-C_2H_2)]$.[7,8] The p.e. spectra for the nickel complexes presented here contain more detailed information than the isoelectronic Co analogues, which allows a more complete discussion of the alkyne–metal interaction.

Experimental

The title compounds were prepared according to the literature methods.[9] Further purification by sublimation *in vacuo* was carried out before running the spectra. He^I (21.217 eV) and He^{II} (40.814 eV) excited p.e. spectra were measured on a Perkin-Elmer PS-18 spectrometer modified for He^{II} measurements by inclusion of a hollow cathode discharge lamp which gives a high photon flux at He^{II} wavelengths (Helectros Development). The spectrometer was connected on-line to a MINC 23 computer (Digital Equipment) by an interface built in our laboratory. Data acquisition was carried out by several sweeps (3—10) over 500 distinct channels. Typical sweep times were 5—10 min. The ionization energy (i.e.) scale was calibrated by reference to peaks due to admixed inert gases (Xe–Ar) and to the He^I $1s^{-1}$ self-ionization.

Results

The He^I excited p.e. spectra of (1) and (2) are reported in Figures 1 and 2 respectively and the i.e.s are reported in the Table. The two spectral patterns show relevant differences which correlate with the electronegativity of the R substituents; there is a general shift toward higher i.e.s in the spectrum of (2) compared with that of (1). The magnitude of this shift, however, is not the same for each band, thus giving rise to different band envelopes for (1) and (2). The spectral region beyond 11.5 eV is more complex for (2) because of the presence of ionizations from the fluorine lone pairs and C–F bonding molecular orbitals (m.o.s) which overlap extensively with the features attributable to the inner π and σ m.o.s of the C_5H_5 rings and to the alkyne σ backbone m.o.s. A detailed assignment of this spectral region is not possible. In Figure 2 the He^{II} excited p.e. spectrum of (2) is also reported; note the relevant loss of relative intensity for bands D, E, F, and G with respect to bands A, B, and C.

Discussion

The spectrum shown in Figure 1 for (1) may be compared with the previously reported spectrum of $[\{Co(CO)_3\}_2(\mu-C_2H_2)]$.[7,8] In the case of (1) the spectrum shows a number of features which are not evident in the cobalt analogue: in addition to the presence of bands related to the outermost π m.o.s of the two C_5H_5 rings (corresponding to e'_1 m.o.s of the free anion of D_{5h} symmetry), the broad band centred at 8.74 eV found in the cobalt complex is split into several components in (1). We can explain the presence of more bands in the present case in terms of the higher effective nuclear charge of Ni compared to Co; this stabilizes the $3d$ Ni atomic orbitals (a.o.s) which strongly mix with outer π C_5H_5 levels.[10] As a consequence,

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† *Non-S.I. unit employed:* 1 eV = 1.602 × 10^{-19} J.

Table. Ionization energies (eV) for [{Ni(η-C_5H_5)}$_2$(μ-C_2H_2)] (1) and [{Ni(η-C_5H_5)}$_2${μ-$C_2(CF_3)_2$}] (2)

Band system	(1)	(2)	Assignment
A	6.85	7.5	Ni–Ni bonding m.o.
B	7.17	7.77	Ni–alkyne back-bonding m.o.s
C	8.2	9.0	Ni 3*d* non-bonding levels
D	8.9	9.4	Ni–C_5H_5 bonding m.o.s
E	9.2	9.9	
F	9.8	10.6	
G	10.9	11.3	π alkyne m.o.s

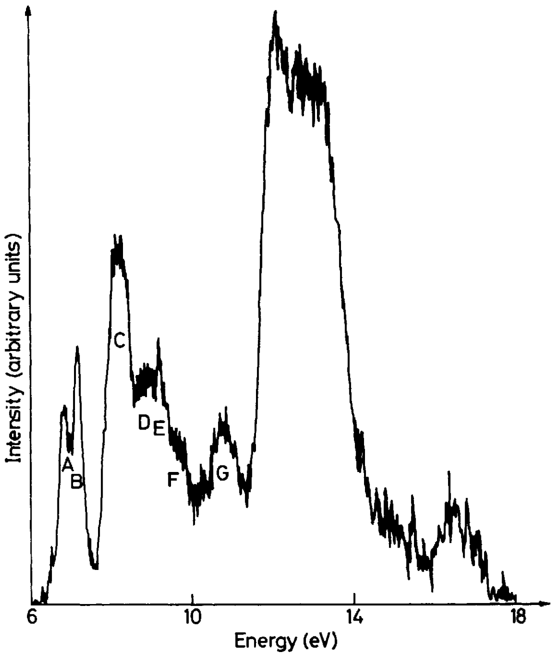


Figure 1. [{Ni(η-C_5H_5)}$_2$(μ-C_2H_2)] He^I excited p.e. spectrum

some 3*d* based m.o.s acquire Ni–C_5H_5 antibonding character, and become resolved from 3*d* ' atom-like ' m.o.s.

We can tentatively assign the p.e. bands in (1) and (2) by a direct comparison with the p.e. bands in closely related systems, such as [{Ni(η-C_5H_5)}$_2$(μ-CO)$_2$] [11] and various nickel cyclopentadienyl complexes.[10] On this basis, band C can be assigned to Ni 3*d* non-bonding levels, and most of the components of bands D, E, and F to the Ni–C_5H_5 bonding m.o.s. This assignment is also supported by the analysis of the variations in relative intensity of bands C, D, and F on going from the He^I to the He^{II} source (see Figure 2). The increase in intensity of band C in the He^{II} spectrum is indicative of a strong contribution of the 3*d* a.o.s to the corresponding m.o.s.[12]

Comparison of band G for (1) and (2) with data from [{Co(CO)$_3$}$_2$(μ-C_2R_2)] [7,8] suggests that this band can be assigned to the π alkyne m.o.s.

In order to establish the origin of bands A and B we refer to the qualitative orbital interaction diagram for (1) shown in Figure 3. This diagram has been built up by mixing together the valence basis sets of the bent fragments {Ni(η-C_5H_5)}$_2$ and C_2H_2 using simple symmetry and overlap considerations. The m.o.s of these interacting fragments are labelled according to the irreducible representations of the C_{2v} point group and the symbols $\perp$ and $\parallel$ refer to the alkyne plane. Only the outermost m.o.s of the {Ni(η-C_5H_5)}$_2$ fragment are individually considered while the Ni 3*d* non-bonding a.o.s ($2a_1 + 2b_2 + a_2 + b_1$ symmetry combinations) and the Ni(η-C_5H_5) bonding m.o.s ($a_1 + a_2 + b_1 + b_2$) are combined in a single block.

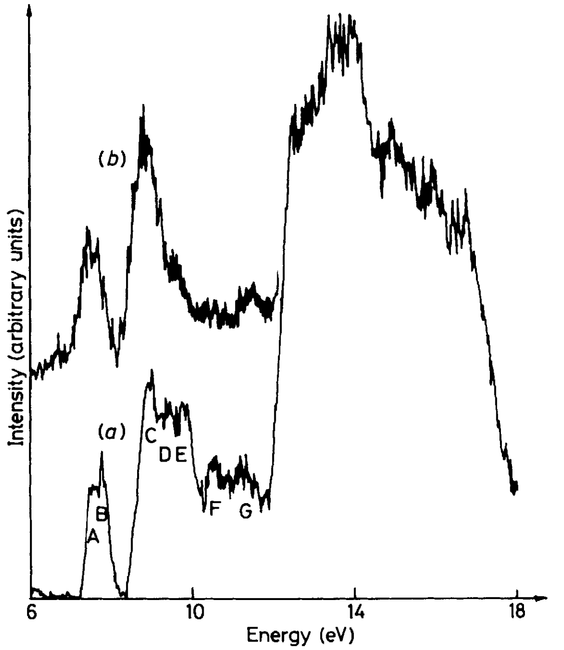


Figure 2. [{Ni(η-C_5H_5)}$_2${μ-$C_2(CF_3)_2$}]: (*a*) He^I excited p.e. spectrum, (*b*) low i.e. region of He^{II} excited p.e. spectrum

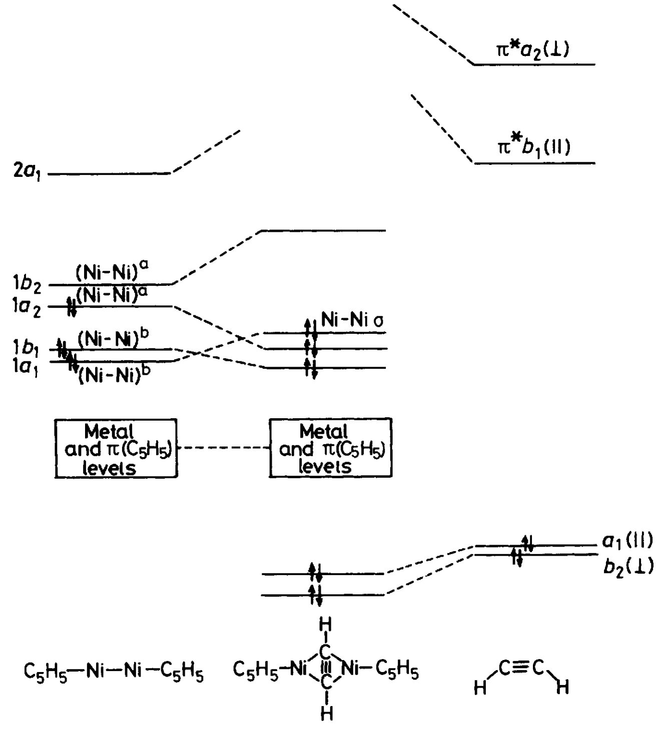
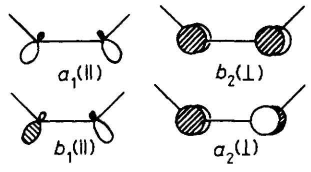


Figure 3. Orbital interaction diagram for [{Ni(η-C_5H_5)}$_2$(μ-C_2H_2)] from its constitutive {Ni(η-C_5H_5)}$_2$ and C_2H_2 fragments

The frontier m.o.s of the {Ni(η-C_5H_5)}$_2$ fragment refer to those reported by Thorn and Hoffmann [13] for the isolobal and isoelectronic {Co(CO)$_3$}$_2$ fragment. The $2a_1$ virtual level, in our case, lies at very high energy since the two C_5H_5 rings have replaced six carbonyl groups.[14] The $1a_1$ and $1b_1$ m.o.s are bonding and the $1a_2$ and $1b_2$ m.o.s are mainly antibonding with respect to the Ni–Ni interaction but they are all antibonding with respect to the Ni–C_5H_5 interaction (see Figure 3).

The pertinent frontier m.o.s of the bent alkyne fragment consist of the nearly degenerate $\pi(a_1 + b_2)$ occupied and of the empty $a_2(\perp)$ and $b_1(\parallel)$ π^* m.o.s (see below).



The overall interaction between the two fragments may be conveniently divided into two contributions: alkyne→metal donation and metal→alkyne back-donation. The a_1 and b_2 type m.o.s will be involved in the former interaction while the a_2 and b_1 m.o.s will contribute to the back-donation. The alkyne $b_2(\perp)$ m.o. contributes to a greater extent than the $a_1(\parallel)$ m.o. to the alkyne→metal donation because of the energy difference between the acceptor $1b_2$ and $2a_1$ m.o.s of the $\{Ni(\eta\text{-}C_5H_5)\}_2$ fragment; however, the filled alkyne $a_1(\parallel)$ m.o. is also stabilized by mixing with the $1a_1$ occupied m.o. of $\{Ni(\eta\text{-}C_5H_5)\}_2$. As a consequence both, $a_1(\parallel)$ and $b_2(\perp)$ are expected to be similarly stabilized in the complex, which explains the observation of one band (G) from these orbitals. Both $1b_1$ and $1a_2$ m.o.s, which are occupied in the $\{Ni(\eta\text{-}C_5H_5)\}_2$ fragment, participate in metal→alkyne back-donation; simple overlap considerations would favour back-donation to the $\pi^*a_2(\perp)$ m.o., but energy matching considerations result in a similar stabilization of $1a_2$ and $1b_1$ m.o.s in the whole molecule. *Ab initio* calculations on $[\{Ni(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_2H_2)]$ [15] and $[\{Co(CO)_3\}_2(\mu\text{-}C_2H_2)]$ [7] (including in this case relaxation effects also) strongly support this view and both demonstrate that the direct metal–metal interaction involves the highest occupied molecular orbital (h.o.m.o.). The above considerations taken as a whole lead us to propose the assignment of band envelope A + B (Figures 1 and 2) to ionizations from the three outermost m.o.s described above. Furthermore, we can tentatively assign band A of (1), on the basis of intensity arguments, to the ionization from the m.o. having Ni–Ni bonding character.

Further information on the bonding/back-bonding mechanism can be obtained by analyzing the reported p.e. data for the CF_3 derivative (2). In Figure 4 is shown the expanded-scale spectra of the first region for (1) and (2). The scale of (2) has been shifted by about 0.7 eV in order to match the C bands (related to ionizations from 3*d* metal-like m.o.s) in the two spectra. We can observe that all band maxima (except G) are similarly shifted toward higher i.e.s in (2). The changes in the relative intensity, however, reflect minor differences in the shift of each ionization contributing to the overall envelope. It is important to note, however, the unexpectedly small shift of band G (0.4 eV). This is quite surprising because the CF_3 substitution would be expected greatly to affect the alkyne π ionizations. Thus, simple inductive arguments cannot explain this experimental result. In our opinion, a larger back-donation in (2), derived from lower-lying π^* alkyne m.o.s, is reasonable and this would result in destabilization of the π alkyne m.o.s because of the accumulation of negative charge on the alkyne and reduction of the C≡C bond order.[16]

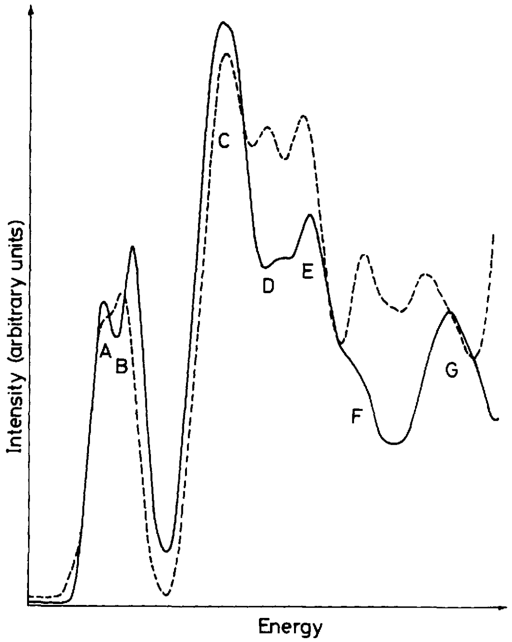


Figure 4. Expansion of the first spectral region of $[\{Ni(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_2H_2)]$ (——) and $[\{Ni(\eta\text{-}C_5H_5)\}_2\{\mu\text{-}C_2(CF_3)_2\}]$ (— — —). The spectra were smoothed and shifted in order to match the C bands

Conclusions

The reported p.e. study gives a new interesting insight into the mechanism of the interactions between an alkyne and two metal centres. In particular, for the first time, p.e. spectral features (bands A and B) which are related to ionizations from m.o.s involved in metal→alkyne back-donation have been detected. Furthermore, the analysis of the CF_3 derivative provides further evidence for the dominant role of the back-bonding interaction in the metal–alkyne bond. This is in complete agreement with similar results obtained for an alkyne bound to three or four metallic centres.[5,17,18] Finally, the observation that the CF_3 substituent effects transmit over the whole molecule, as seen by the similar shift of all bands to the same extent (except G), suggests a very delocalized electronic distribution for these molecular systems.

Acknowledgements

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