

The Metal–Alkene Bond in Di- μ -chloro-tetra(ethene)dirhodium(I): Direct Evidence for the Dewar–Chatt–Duncanson Model Using X-Ray Emission and X-Ray Photoelectron Spectroscopies

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Changes in the carbon- K_{α} X-ray emission spectrum of ethene upon complex formation together with the alignment of the X-ray photoelectron spectrum of the complex show that ethene both donates charge from the π orbital to rhodium 4d orbitals and also forms bonds in which charge is 'back-donated' from the rhodium 4d orbitals to the alkene π^* orbital, as predicted by the Dewar–Chatt–Duncanson model.

Dewar^{1a} and later Chatt and Duncanson^{1b} proposed that the bond between a transition metal and an unsaturated ligand had two complementary components: donation of electron density from the π bond of the alkene to a suitable vacant

hybrid orbital on the metal and back-donation from the filled metal d orbitals to the empty π^* orbital of the alkene. Whilst this elegant model has provided a rationalisation of many physical and spectroscopic properties of alkene complexes²

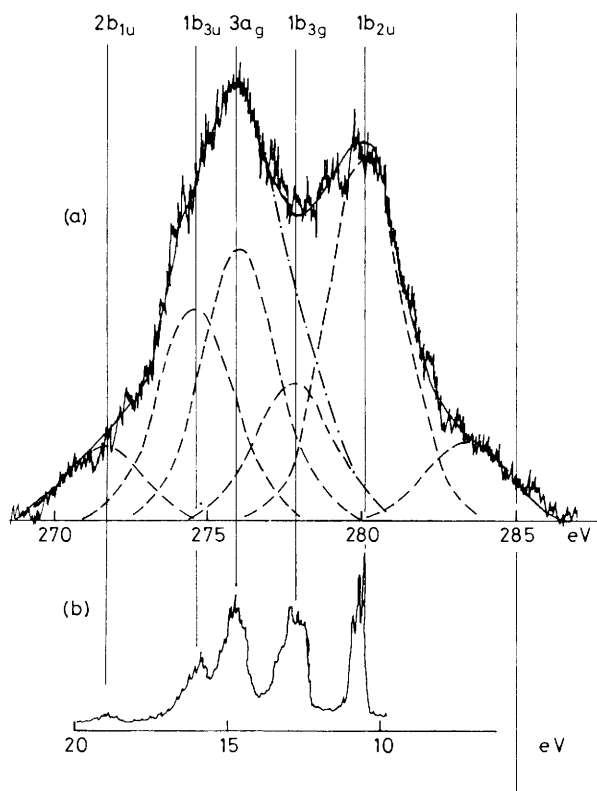


Figure 1. (a) Carbon- K_{α} X-ray emission spectra of ethene (89 K). Dashed lines indicate proposed components peaks; - - - - sum of ' σ ' peaks; ——— sum of all component peaks. (b) UP spectrum of ethene from Ref. 9.

direct evidence for this synergic bonding between the metal and the alkene ligand is lacking. Provided that Koopmans' theorem is obeyed, or if it is not, provided that relaxation effects in related compounds can be assumed identical, the X-ray photoelectron and X-ray emission spectroscopies, which map out the ionisation energies of occupied orbitals and probe the bonding roles of specific atomic orbitals, respectively,³ should be able to provide such evidence. The results of Khel'met *et al.*⁴ were however inconclusive since comparison of the carbon- K_{α} emission spectrum (in which the fine structure of the X-ray peak reflects carbon 2p participation in specific molecular orbitals) of the $[(C_2H_4)_2RhCl]_2$ complex was made with the carbon- K_{α} spectrum of ethene taken by Mattson and Ehlert.⁵ These authors used direct electron bombardment to excite their spectrum which resulted in rather intense high energy ($K_{\alpha 3,4}$) satellites being found in the region in which any evidence of 'back-bonding' would be sought.

For the experiments described here the di- μ -chlorotetra-(ethene)dirhodium(i) complex was made in the usual way⁶ and stored under dry nitrogen at near 0 °C until required for use. This particular complex was chosen because of its high ethene content and the simplicity of its structure. Carbon X-ray spectra were measured with a Philips PW 1410 X-ray fluorescence spectrometer in which emission was excited by means of a C.G.R. Elent-10 gas-discharge open-window X-ray tube (3 mA, 5 kV, *ca.* 4×10^{-2} Torr air). The complex was mounted by pressing it into a fine copper mesh. To measure the C- K_{α} spectrum of ethene the gas was continuously bled into the spectrometer and frozen onto a cooled probe at *ca.* 89 K.⁷ The carbon spectra were diffracted using a lead myristate soap film 'pseudo-crystal' (2d = 7.90 nm) and calibrated using the potassium L_i and L_{η} lines. These

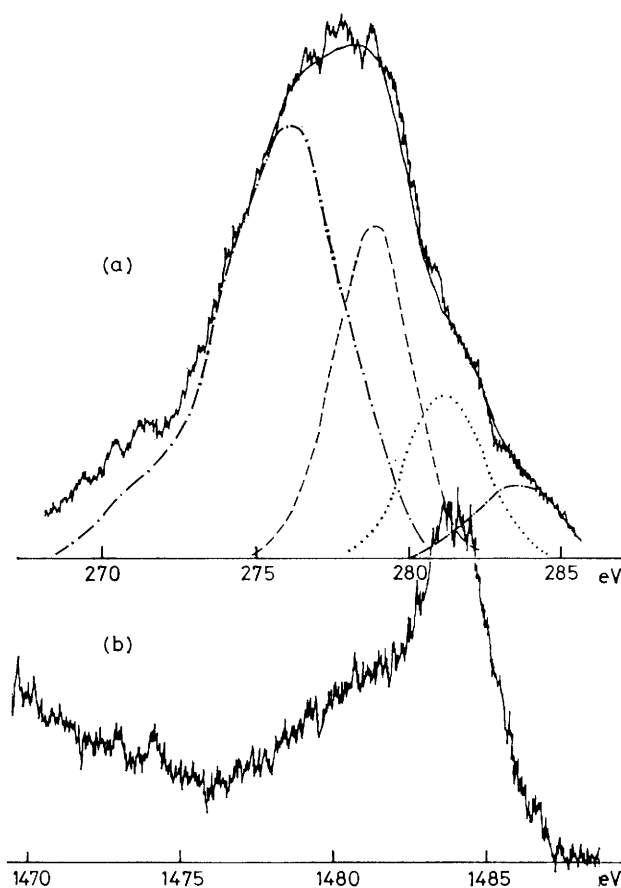


Figure 2. (a) Carbon- K_{α} emission spectra and (b) XP spectrum from the $[RhCl(C_2H_4)_2]_2$ complex aligned using the C 1s photoelectron kinetic energy of 1202.5 eV. The lines indicate the following: ——— σ and high energy satellite peaks from Figure 1; - - - - displaced π peak; ····· 'back-bonding' peak (note alignment with XP spectrum peak at 1485 eV corresponding to Rh 4d).

lines were also used to determine the peak profile, which was Gaussian (to within experimental error) with a full width at half height of 3.0 eV. Other spectra, Rh- $L_{\beta 2,15}$ ($4d \rightarrow 2p_{3/2}$), and Cl- $K_{\beta 1,3}$ ($3p \rightarrow 1s$), were measured on the same equipment but using a conventional Cr anode X-ray tube (50 mA, 50 kV) and ethylenediamine-D-tartrate 200 (2nd order) and silicon 111 crystals, respectively.

The C- K_{α} spectrum for ethene is shown in Figure 1. Since the 1s ionisation energy for carbon in ethene is 290.8 eV⁸ the ultraviolet photoelectron (UP) spectrum⁹ can be aligned as shown in Figure 1. Thus the peak at 280.0 eV can be identified as due to the π ($1b_{2u}$) orbital whilst the broad peak at 276.0 eV arises from C 2p character in the C-H ($1b_{3g}$), C-C ($3a_g$), and C-H ($1b_{3u}$) σ bonding molecular orbitals. A little C 2p character in the C-C ($2b_{1u}$) molecular orbital gives rise to the feature at 271.6 eV. The deconvolution suggested in Figure 1 is based on Gaussian curves (full width at half height, 3 eV) located at positions indicated by the UP spectrum. The remaining peak at 283.5 eV is due to a high energy satellite, caused by relaxation of a doubly ionised carbon atom.

The C- K_{α} spectrum for the complex is shown in Figure 2. As can be seen there are dramatic changes in the π region. The deconvolution is based on the σ profile (the sum of the σ peaks) and also the high energy satellite peak from Figure 1. For the remainder of the spectrum it is necessary to

propose two peaks as shown in Figure 2. The dashed line would seem to correspond to the π orbital of ethene, but displaced to a lower energy (corresponding to a higher bonding energy). A new peak (dotted, Figure 2) is found at 281.2 eV. Core and valence orbital ionisation energies were measured using a Vacuum Generators ESCA 3 (Mk 1) X-ray photoelectron (XP) spectrometer (unmonochromatised Al- $K_{2,1,2}$ radiation: 10 kV, 10 mA; 2×10^{-9} Torr). The aligned XP valence-band spectrum of the complex is also shown in Figure 2. The Rh- $L_{\beta_{2,15}}$ spectrum indicates that Rh 4d character is found in orbitals in the 1479–1486 eV region with a peak at ca. 1484 eV. Chlorine 3p character (as shown by the Cl- $K_{\beta_{1,3}}$ spectrum) is located at ca. 1481 eV. From the intensity of the peak at 1470 eV in the XP spectrum which is due to Cl 3s orbitals and the $2a_g$ orbital of ethene (mostly C 2s character), it is possible to estimate the magnitude of peaks in the 1478–1486 eV region due to Cl 3p and C 2p character and so to conclude that this part of the XP spectrum is almost entirely due to Rh 4d character.

The new peak found in the spectrum of complexed ethene is thus due to molecular orbitals with both Rh 4d and C 2p character and is therefore a direct indication of the formation of 'back-donation' bonds between the least tightly bound 4d rhodium orbitals and the π^* orbitals of ethene. Similarly the alignment of the displaced π peak in the complex and the shoulder in the XP spectrum at 1481 eV provides direct evidence for the formation of bonds between the ethene π bonds and 4d rhodium orbitals. This contrasts with the behaviour of alkenes in complexes with $\text{Fe}(\text{CO})_4$ where little or no stabilization of the bonding π orbital is found.¹⁰ Evidence for Rh 5p involvement in the forward and back donation components was also sought but not found. This result confirms the conclusions of SCF- X_2 -SW calculations on the related complex $\text{K}[\text{PtCl}_3(\eta\text{-C}_2\text{H}_4)]^{\text{II}}$ which have suggested that the Chatt–Duncanson bonding picture overestimates the degree of involvement of the Pt 6s and 6p orbitals in metal–alkene binding.

X-Ray emission and X-ray photoelectron spectra thus confirm in a simple and dramatic way that the widely used model for the metal–alkene bonding is in fact correct.

The authors thank the S.E.R.C., The Royal Society, and The Central Research Fund of London University for grant for the purchase of equipment and Professor Henke (University of Hawaii) for the gift of a lead myristate pseudo crystal. D. S. U. thanks Scientific Affairs Division of N.A.T.O. for a research fellowship and J. A. expresses her gratitude to the S.E.R.C. and the Health and Safety Executive for a C.A.S.E. award.

Received, 28th June 1982; Com. 752

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