

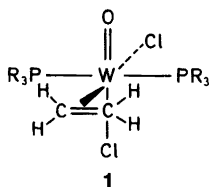
An Electronic Interpretation of the Structure of $W(O)Cl_2(CH_2=CH_2)(PMePh_2)_2$

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Recently, the crystal structures of the first examples of metal complexes containing both simple olefins and terminal oxo ligands were published.¹ The complexes were formed by reaction of olefins with *cis-mer*- $W(O)Cl_2(PMePh_2)_3$, with liberation of one phosphine ligand; the structure of the ethylene complex (**1**) is shown below:¹



Species containing olefins bound to transition metals have often been suggested as important intermediates in many oxidation reactions but never observed, for example in epoxidation reactions³ and osmium tetroxide oxidations.⁴ However, it has recently been shown that another mechanism may operate in the latter examples.⁵

*All calculations have been performed using the extended Hückel method and the parameters used are available from the literature.^{6b} The bond lengths and angles of **1** were taken from Ref. 1. R = H in the phosphine.

The purpose of this letter is to discuss the structure and some of the spectroscopic and chemical properties of **1** using the frontier orbital approach, symmetry arguments and extended Hückel calculations.^{6,*}

Let us start with the frontier orbitals of $W(O)Cl_2(PMePh_2)_2$ (an ML_5 fragment) shown to the left in Fig. 1. $W(O)Cl_2(PR_3)_2$ has d^2 configuration, with the HOMO as an approximately non-bonding tungsten d_{xy} /weakly tungsten-chloride π antibonding orbital. The rest of the t_{2g} set is split substantially by the oxo ligand into the e set, which is strongly tungsten-oxygen antibonding, giving the LUMOs of the system. The remaining HOMOs depicted in Fig. 1 are mainly of p character at the ligands, except for the last one in which a small percentage of d_{xy} at tungsten mixes in. Contour plots of those orbitals which might be expected to be involved in the interaction with an olefin are shown in Fig. 2.

It appears from Figs. 1 and 2a that the HOMO of $W(O)Cl_2(PR_3)_2$ has the right symmetry to coordinate an olefin parallel to the P-W-P bond by interaction with the π^* orbital of the olefin, as π -type back bonding. One of the LUMOs and the third LUMO, symmetric with respect to the yz plane (Figs. 1 and 2b), then have the right symmetry to interact with the π orbital of an olefin. The interaction diagram for $W(O)Cl_2(PR_3)_2$ with an olefin is shown in the remaining part of Fig. 1,

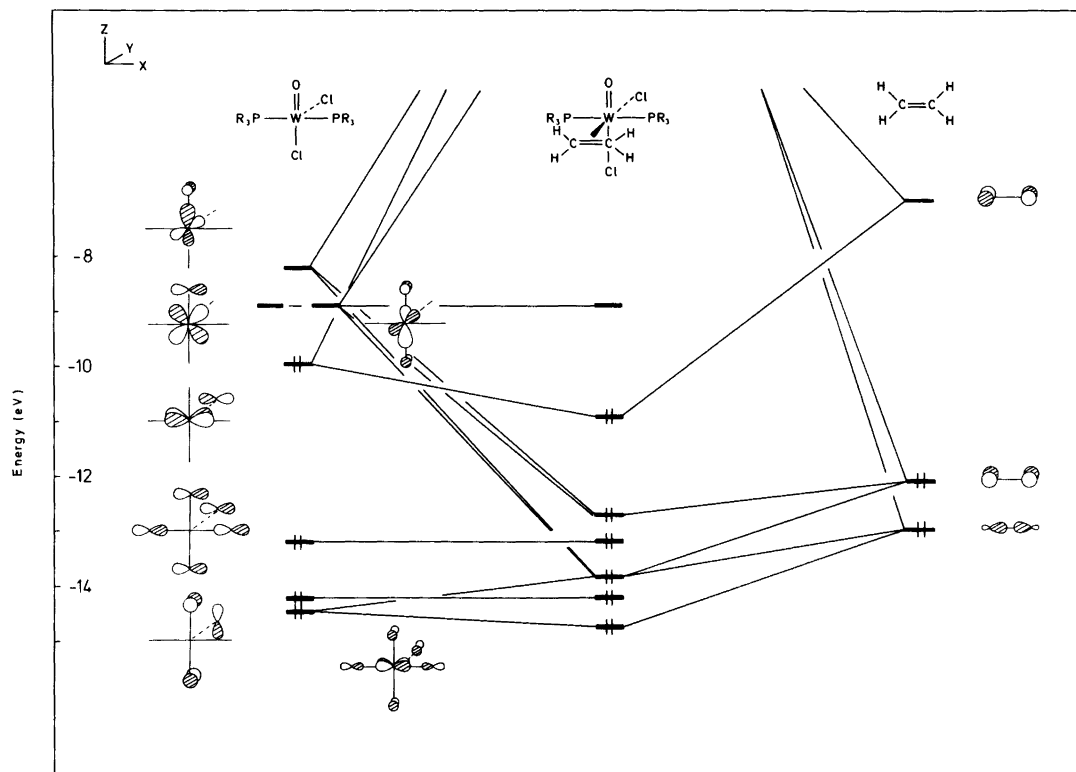


Fig. 1. Interaction diagram for the formation of the $W(O)Cl_2(CH_2=CH_2)(PR_3)_2$ complex from $W(O)Cl_2(PR_3)_2$ (to the left) and $CH_2=CH_2$ (to the right).

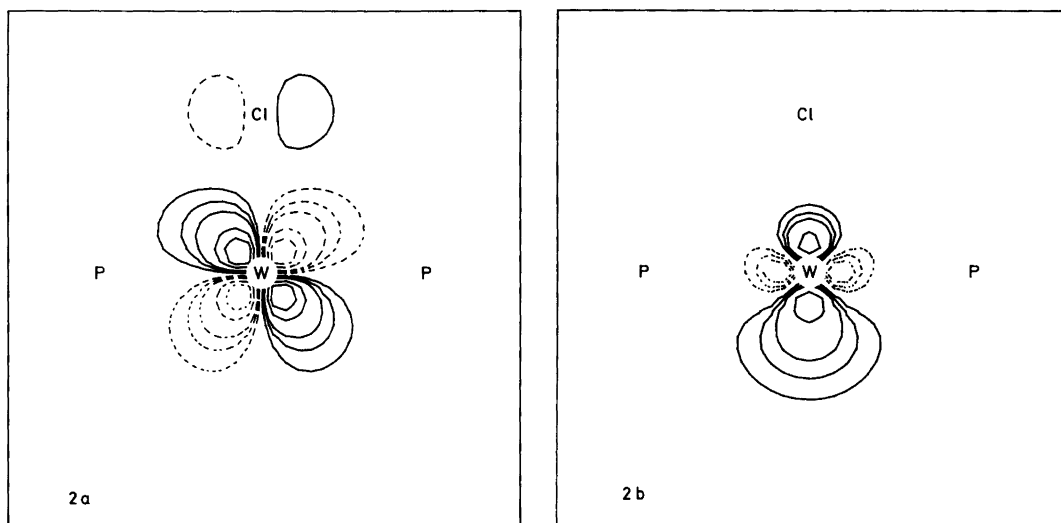
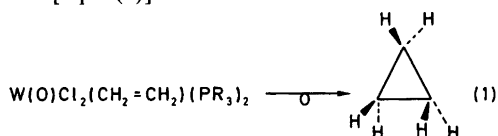


Fig. 2. Plot of HOMO (2a) and LUMO (2b) of $W(O)Cl_2(PR_3)_2$. The contour levels of ψ are 0.30, 0.20, 0.10, 0.07 and 0.04. The orbitals are plotted in the xy plane.

and according to the discussion above it shows stabilization of the olefin at the tungsten center. The interaction diagram indicates that donation of electrons from the olefin π orbital into the two tungsten symmetric unoccupied orbitals, and π back-donation of electrons from the tungsten d_{xy} orbital into the π^* -acceptor orbital of the olefin are both important for the stabilization of the complex.

The rotation barrier for ethylene rotation about the tungsten-ethylene bond can be calculated, by summing the orbital energies of the occupied orbitals, to be 18 kcal mol^{-1} , supporting the experimental results.¹ The overlap population between tungsten and the olefinic carbons in **1** is 0.118, whereas it is 0.026 and -0.009 when the olefin is parallel to the tungsten-oxo bond, thereby indicating stronger binding in the first case. Using the isolobal principle⁷ for $\text{W}(\text{O})\text{Cl}_2(\text{CH}_2=\text{CH}_2)(\text{PR}_3)_2$, the organic counterpart of this complex can be shown to be cyclopropane [eqn. (1)].



From the character of the frontier orbitals of **1** it is seen that an epoxidation of the olefin, similar to that observed with e.g. $\text{MoO}(\text{O}_2)_2$ ^{3c} and CrO_2Cl_2 ,^{4a} seems improbable since the olefinic π^* orbital is involved in π back-donation from the tungsten d_{xy} orbital which is thereby not available directly for an interaction with the orbitals at the oxygen. This type of interaction has otherwise been suggested as an important factor in the epoxidation of olefins by $\text{MoO}(\text{O}_2)_2$ complexes.^{3c} It should also be mentioned that there is experimental evidence that it is the peroxy oxygens,

and not the oxo oxygen, that are involved in epoxidation by $\text{MoO}(\text{O}_2)_2$ complexes.⁸

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