

Electronic Mechanisms Associated with Bond-Stretch Isomerism in Transition Metal Complexes

Yves Jean,^{*a} Agusti Lledos,^{a,b} Jeremy K. Burdett,^{*c} and Roald Hoffmann^{*d}

^a Laboratoire de Chimie Théorique (CNRS U.A. no. 506), Université de Paris-Sud, 91405 Orsay-Cedex, France

^b Departament de Química-Física, Universitat Autònoma de Barcelona, Bellaterra, Barcelona, Spain

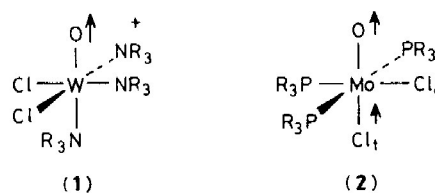
^c Department of Chemistry, University of Chicago, Chicago, Illinois 60637, U.S.A.

^d Department of Chemistry, Cornell University, Ithaca, New York 14853, U.S.A.

Two electronic mechanisms are presented which can explain the existence of bond-stretch isomerism in transition metal complexes: the first entails a real level crossing, and the second, best regarded as a second-order Jahn–Teller effect, has links with bond localization problems in allyl anion and benzene.

It has become clear over the past few years that a new type of isomerism exists. There are now molecules in the solid state and also in solution which interconvert with varying degrees of ease, and whose only structural difference is a dramatic difference in the length of one or several bonds. We call this bond-stretch isomerism after earlier theoretical work dealing with main group systems.¹ (1) and (2) show some relevant bond lengths in two sets of molecules studied by Wieghardt and colleagues,² and by Chatt, Manojlović-Muir, and Muir, respectively.³ The second group used the term 'distortional isomerism' to describe the effect which so far is restricted to transition metal examples as far as crystallographic characterization is concerned. Notice in (1) and (2) the large difference in M–O distance. These molecules are representatives of a class of M^{IV,V} (M = Mo, W) compounds which may be made in 'blue' and 'green' forms, and show different $\nu(\text{MO})$ frequencies. Also known are some isoelectronic rhenium nitrides which show large differences in their ¹⁵N chemical shifts.⁴ In this communication we describe two mechanisms which may give rise to this effect, and how the nature of the other ligands, co-ordinated to the metal, influences the electronic picture.

One possibility is the crossing of two electronic states, with different bonding properties, as the M–O linkage is stretched. Figure 1 shows how this may occur in the *cis*-(WOC₂H₄)³⁻ model complex in an idealized octahedral geometry. The *xy* orbital is not involved in interaction with any orbital located on the moving oxygen atom, and so remains unchanged in energy on distortion. However *y*₂ and *x*₂ orbitals are involved



(1-a)	(1-b)	(2-a)	(2-b)
W–O 1.719 (18)	1.893 (20) Å	Mo–O 1.676 (7)	1.803 (11) Å
		Mo–Cl _c 2.551 (3)	2.426 (6) Å

