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Elian M & Hoffmann R. Bonding capabilities of transition metal carbonyl fragments. *Inorg. Chem.* 14:1058-76, 1975.
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The energy ordering, symmetry, and extent in space of the valence molecular orbitals of a range of geometries of $M(CO)_3$, $M(CO)_4$, and $M(CO)_5$ fragments, where M is a transition metal center, are analyzed in detail. The properties of the fragment orbitals are then used to examine the ability of the fragments to interact with other ligands as well as the geometrical preferences of the isolated fragments. [The *SCI*® indicates that this paper has been cited in over 505 publications.]

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The coauthors of this article came to inorganic chemistry, and specifically to organometallic chemistry, in different ways. Mihai Elian began his studies in physical organic chemistry with the late Costin Nenitzescu in Bucharest. In 1969 Elian visited the group of E.O. Fisher in München, and there was introduced to the joys of organometallic chemistry. Roald Hoffmann began as a theoretical inorganic chemist with W.N. Lipscomb, but from the time of his collaboration with R.B. Woodward he concentrated on organic molecules. At Cornell University, his group developed an approach to organic molecules and reaction intermediates that was based on the extended Hückel method, but more importantly on a frontier orbital perspective, a singling out of the higher occupied and lower unoccupied orbitals of a molecule as controlling electronic structure and reactivity. The extended Hückel method had limitations, but it was extraordinarily transparent and lent itself well to a perturbation theory analysis. *Explanations* were easy to extract from it, couched in simple terms, based on bonding, symmetry, and overlap.

In the early 1970s the Hoffmann group became interested in inorganic chemistry. Their entry point was the chemistry of sulfur and phosphorus, and they were greatly aided by Earl Muetterties, who had just joined the Cornell faculty. He helped the group appreciate the beauties of inorganic stereochemistry and introduced them to transition metal chemistry. Inorganic chemistry, especially organometallic chemistry, was in the air. It was high time to learn it, to overcome barriers to drawing d electrons and to counting electrons (what trivial obstacles we create for ourselves!).

The Hoffmann group began, gingerly at first, to look at transition metal complexes. It was helped by the programming of a new interpretative tool, the fragment molecular orbital analysis, brought to the group by Hiroshi Fujimoto.[1,2] This method seemed ideally suited to typical problems in organometallic chemistry: for instance, the nature of the bonding in (cyclooctadiene)-$Cr(CO)_4$ vs. $Fe(CO)_3$. Obviously, one should divide the molecule into an organic piece (cyclooctadiene) and an inorganic one {$Cr(CO)_4$, $Fe(CO)_3$}. Any differences in bonding would emerge from a reconstitution of the composite molecule from its fragments. That's, in fact, carried out in part of this paper.

Elian came to Cornell as a postdoctoral associate just at the time the inorganic work took off. We worked hard together, building piece by piece a library of most of the important fragments of inorganic chemistry, in every conceivable geometry. After this library was in place, it was simple to implement the reconstruction of the bonding in most any inorganic or organometallic molecule. And in the course of this analysis we grew aware of a remarkable similarity between the orbitals of inorganic and organic molecular building blocks. In time this became the isolobal analogy.[3]

1. **Hoffmann R, Fujimoto H, Swenson J R & Wan C-C.** Theoretical aspects of the bonding in some three-membered rings containing sulfur. *J. Amer. Chem. Soc.* 95:7644-50, 1973. (Cited 95 times.)
2. **Fujimoto H & Hoffmann R.** A molecular orbital study of the addition of singlet methylene to butadiene. *J. Phys. Chem.* 78:1167-73, 1974. (Cited 70 times.)
3. **Hoffmann R.** Building bridges between inorganic and organic chemistry (Nobel Lecture). *Angew. Chem. Int. Ed.* 21:711-24, 1982. (Cited 275 times.) (Also published as *Angew. Chem.* 94:725-38, 1982. [Cited 135 times.])

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