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Review

M≡E and M=E complexes of iron and cobalt that emphasize three-fold symmetry (E≡O, N, NR)

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JCP is grateful to his friend and colleague Professor Harry Gray, who continues to be an inspirational mentor and has made discussions of the electronic structures of metal oxos, imides, and nitrides at once so enjoyable and insightful over the course of the past decade. Happy Birthday Chief!

ABSTRACT

Mid-to-late transition metal complexes that feature terminal, multiply bonded ligands such as oxos, imides, and nitrides have been invoked as intermediates in several catalytic transformations of synthetic and biological significance. Until about ten years ago, isolable examples of such species were virtually unknown. Over the past decade or so, numerous chemically well-defined examples of such species have been discovered. In this context, the present review summarizes the development of 4- and 5-coordinate Fe(E) and Co(E) species under local three-fold symmetry.

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1. Introduction

Multiply bonded species of the late transition metals (M≡E and M=E, where E = O, N, NR, CR) have been postulated as key intermediates in many synthetic and enzymatic transformations [1–8]. These transformations include, for example, olefin epoxidation and aziridination [9–14], C–H bond oxygenation and amination

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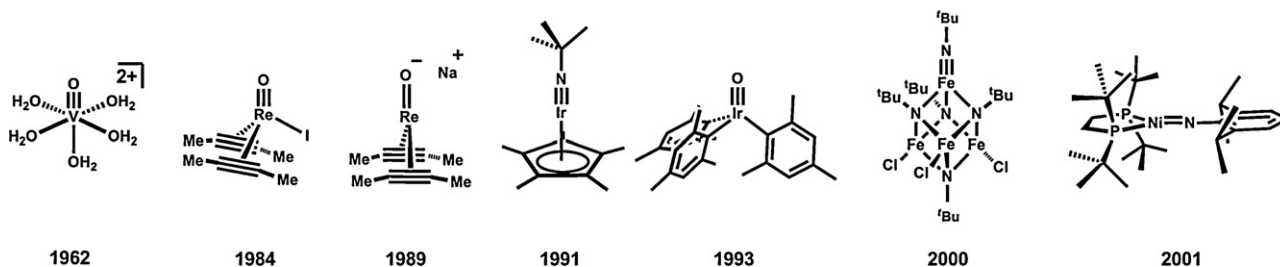 *E-mail address:* jpeters@caltech.edu (J.C. Peters).

Fig. 1. Examples of M≡E and M=E species, with year of publication noted.

[15–19], and e^-/H^+ transfer processes related to nitrogen fixation [20,21]. The diverse multi-electron reactivity exhibited by such species is in part attributed to their multiple bond character, and there has hence been much interest in understanding the electronic structures and reactivity patterns of such species [22–27].

The molecular orbital (MO) picture of complexes of the type C_{4v}-$L_5M(E)$ was developed in the classic study of the d^1 vanadyl ion (VO^{2+}) by Ballhausen and Gray [28] (Fig. 1). This MO picture stressed a large splitting of the t_{2g} orbitals ($\Delta_\pi \approx 13,000\,cm^{-1}$), arising from the presence of a strongly π donating oxo ligand, and the presence of a V≡O triple bond. As a consequence, complexes of the type $L_nM(E)$ should feature *bona fide* multiple bond character, and hence electronic stability, when M(E) π^* orbitals are vacant or only partially filled [1], regardless of local symmetry.

With this generalization in mind, there are at present three well-identified pathways to achieve a reasonable degree of electronic stability in an M≡E or M=E interaction (also abbreviated as M(E)). The most straightforward and hence historically most familiar way is to preserve a low d-electron count at the metal. For a prototypical 6-coordinate metal center that features one terminal multiply bonded ligand $L_5M(E)$, the σ^* and π^* bonding interaction results in the destabilization of four orbitals of d-parentage. It is therefore not surprising that high-valent early transition metals that feature d^0, d^1, or d^2 electron counts have historically dominated the literature of terminal $L_5M(E)$ complexes [29]. To a first order approximation, the π-bond order decreases from 2 to 3/2, 1, and 1/2 as the d^3, d^4, and d^5 configurations are, respectively, populated. Such an approach is of course not limited to complexes of four-fold symmetry. The high stability of complexes such as trigonal bipyramidal (TBP) {(Me_3SiNCH_2CH_2)_3N}V(O) [30] and tetrahedral ($^iPr_2N$)$_3$Cr(N) [31] drives home this point. A second means of achieving electronic stability in M(E) species constitutes using a combination of ligands that are both σ donating and π-accepting.

Synergism in this context can in principle, via orbital mixing, serve to stabilize d-electrons that would otherwise be destabilized via a strong π^* interaction. Such a scenario has been used, for example, to offer an explanation for the unanticipated stability of the d^6 $L_5Pt(O)$ species prepared by Hill and co-workers [32]. A third mode of achieving electronic stabilization for multiply bonded species is to remove donor ligands from the central metal under consideration. This provides a distinct electronic structure that may be able to accommodate a higher number of d-electrons, so long as those electrons do not fill strongly destabilized orbitals. For example, under three-fold symmetry, both 4- and 5-coordinate species can accommodate M(E) species with diverse d-electron configurations (Fig. 2) [6,27,33–35].

Synthetic entry to M(E) complexes featuring higher d-electron counts first surfaced about 25 years ago when Mayer and Tulip isolated and characterized an intriguing Re(O)I(MeC≡CMe)$_2$ complex (Fig. 1) [33]. This was the first well-characterized terminal M(E) multiple bond linkage for a complex formulated as d^4. The Re–O bond distance of 1.697(3) Å in Re(O)I(MeC≡CMe)$_2$ is similar to that of higher valent Re(O) complexes [36], suggesting that the π^* orbitals are not populated. To achieve such stabilization, the Re adopts a distorted geometry that can be crudely described as tetrahedral, with approximate three-fold symmetry about the Re–O bond [37]. The two electron reduction of a related complex, Re(O)I(PhC≡CPh)$_2$, furnished an equally interesting d^6, 3-coordinate [Re(O)(PhC≡CPh)$_2$][Na] species [35]. In this latter complex, partial population of π^* orbitals is presumed to cause elongation of the Re–O bond to 1.756(3) Å, a destabilization that leads to a more reactive metal center (Fig. 1). At a similar time, Meyer and co-workers identified the interesting intermediate-spin, d^4 ruthenium oxo species (bpy)$_2$(py)Ru(O)$^{2+}$ [38–40]. Again, partial population of π^* orbitals was presumed to give rise to a more reactive Ru(O) linkage.
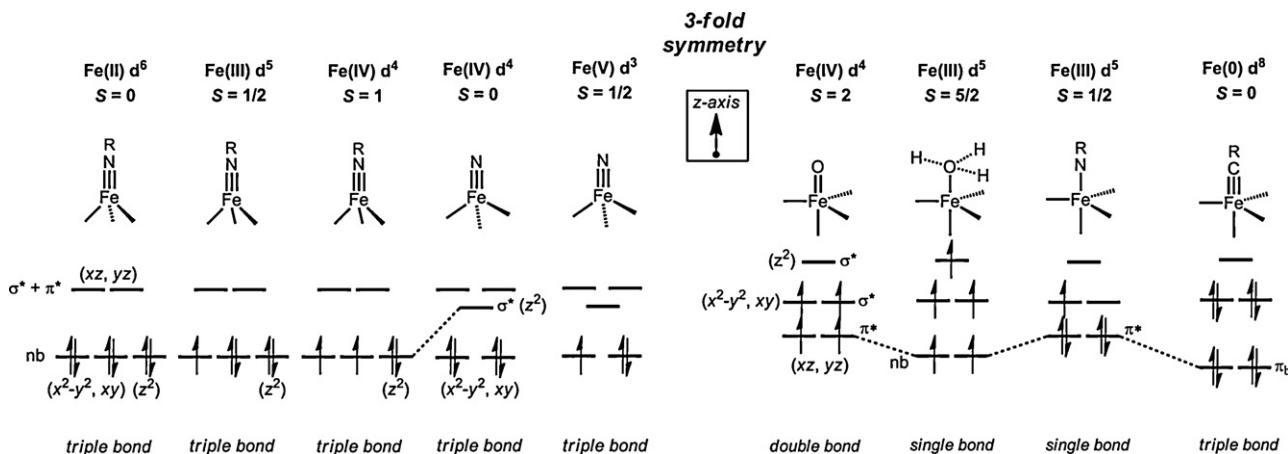

Fig. 2. Qualitative d-orbital splitting diagrams for L_3-Fe(E) and $L'L_3$-Fe(E) structure types discussed throughout the review. The diagram is meant as a guide to the discussion in the text. The relative ordering of the orbital energies for the lower-lying e set (xy, x^2-y^2) and the a_1 orbital (z^2) is not implied for L_3Fe(NR) structures, and are arbitrarily set as degenerate, for simplicity.