

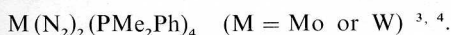
# DIAZENIDO, DINITROGEN AND RELATED COMPLEXES

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**ABSTRACT.** — This paper presents a qualitative molecular orbital picture of the structure and reactivity of diazenido NNR complexes and related molecules including dinitrogen NN, hydrazido NNR<sub>2</sub>, imido, NNR<sub>3</sub>, nitrido N, as ligands. The primary focus is the geometry of the ligands in six and five-coordinate structures and the reactivity of these molecules to acid attack. Specific questions treated are bending at N' and N'', the charge distribution in the coordinated dinitrogen and diazenido ligands, the difference in photochemical reactivity of mono- and bis-dinitrogen complexes, deformations in square-pyramidal and trigonal-bipyramidal diazenido complexes, comparison of nitrosyl and diazenido ligands, and the electronic structure of hydrazido, imido and nitrido complexes.

Current interest in transition metal complexes containing dinitrogen itself, diazenido and other reduced forms of the dinitrogen ligand stems from their potential as models for the biological process of nitrogen fixation, and as nitrogen-fixing catalysts in their own right<sup>1, 2</sup>. Stoichiometric protonation of coordinated dinitrogen to ammonia has been achieved for the well defined complexes



Other interesting alkylation<sup>5</sup> and protonation<sup>6</sup> reactions have yielded ligands containing reduced nitrogen. Our purpose here is to present a systematic molecular orbital analysis of the electronic structure of some dinitrogen, diazenido, and related complexes to aid in understanding their chemistry and structure.

The discussion that we present will be quite qualitative. It is supported by extended Hückel calculations, with parameters described in the Appendix. This computational method has well-known deficiencies, so that the reader should be aware that any detailed numerical outcomes of the calculations should be viewed with caution. Dinitrogen complexes of transition metals have been subject to a number of other theoretical studies<sup>7</sup>.

The nomenclature of coordinated nitrogenic ligands could be charitably described as "diversified". Throughout this paper we will use the verbal descriptor dinitrogen instead of N<sub>2</sub>. Where the symbols N' or N'' appear, they refer to the individual nitrogen atoms respectively adjacent and removed from the metal atom (i. e. M—N'—N''). The NNR ligand will be called "diazenido", NNR<sub>2</sub> "hydrazido", NNR<sub>3</sub> "imido", N "nitrido".

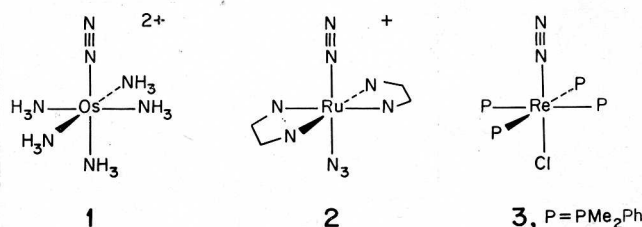
## Six-coordinate mono- and bisdinitrogen complexes

Most dinitrogen complexes are six-coordinate, and the structural details of several of these are known from crystallographic studies<sup>8</sup>. Among these are compounds **1**<sup>8b</sup>, **2**<sup>8c</sup>, and **3**<sup>8d</sup>.

All of these complexes have {MNN}<sup>6</sup> electronic configurations with MNN angles of nearly 180°. Here we have adopted the notation introduced by Enemark and Feltham for nitrosyl complexes<sup>9</sup>. Dinitrogen and diazenido complexes are designated by {MNN}<sup>r</sup> and {MNNR}<sup>r</sup> respectively

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where *r* is the number of electrons associated with metal *d* orbitals and the π\* orbitals of the ligand.



The interaction of N<sub>2</sub> with the square-pyramidal fragment RuCl<sub>3</sub>(PH<sub>3</sub>)<sub>2</sub><sup>-</sup> to form the hypothetical RuCl<sub>3</sub>(PH<sub>3</sub>)<sub>2</sub>N<sub>2</sub><sup>-</sup> complex is shown in Figure 1. There is nothing novel about the molecular orbital scheme given here, but we would like to have the nature of the molecular orbitals well in mind for further discussion. The five-coordinate metal fragment has the typical splitting pattern for square pyramidal complexes<sup>10</sup>. The x<sup>2</sup>-y<sup>2</sup> orbital which is antibonding to all four ligands of the basal plane lies highest, the antibonding combination of the z<sup>2</sup> orbital with the axial ligand lies considerably lower, and the three lowest *d* block molecular orbitals are the *xz*, *xy*, and *yz* which are sigma-nonbonding. The small energy differences in the latter three orbitals arise from varying degrees of π bonding with the ligands. The σ and π\* orbitals of the dinitrogen ligand shown on the right-hand side of Figure 1 are of proper energy and symmetry to interact significantly with the metal fragment<sup>10c</sup>.

The mixing of the sigma orbital of dinitrogen with the z<sup>2</sup> orbital of the square-pyramidal fragment produces bonding and antibonding combinations and results in the typical energy level ordering of an octahedral complex, i. e. with x<sup>2</sup>-y<sup>2</sup> and z<sup>2</sup> (e<sub>g</sub>) above the *xy*, *xz*, and *yz* (t<sub>2g</sub>) orbitals. The π\* orbitals of dinitrogen lie between the e<sub>g</sub> and t<sub>2g</sub> sets in our calculations. These π\* orbitals interact with the *xz* and *yz* orbitals of an ML<sub>5</sub> fragment to give the bonding and antibonding combinations of Figure 1. The *xy*, *xz*, and *yz* orbitals are nearly of equal energy as shown, but the *xy* orbital is expected to lie above the *xz* and *yz* orbitals as the latter are stabilized by interaction with the π\* orbitals of dinitrogen. Our molecular orbital scheme for a dinitrogen complex is thus a typical diagram for an octahedral complex,

