

carried out in the presence of $\text{IrP}_2(\text{NO})_2\text{Br}$, $[\text{IrP}_2(\text{NO})_2]\text{PF}_6$, $\text{IrP}_2(\text{CO})(\text{solvent})^+$, and their Rh analogs. The reactions proceed catalytically, albeit slowly, at 20° . For example, with $[\text{RhP}_2(\text{NO})_2][\text{PF}_6]$ after 170 hr there is a 62% conversion of reactants to products with 126 mol of N_2O produced per mole of Rh.¹⁸ $\text{IrP}_2(\text{NO})\text{Br}_2$, $\text{CoP}_2(\text{NO})_2\text{Br}$, and $[\text{CoP}_2(\text{NO})_2][\text{PF}_6]$ were found to be inactive.

The anomalous reactivity and catalytic properties of certain four- and five-coordinate dinitrosyl complexes suggest to us that many of the "20-electron" dinitrosyls, at least while intermediates in these reactions, may be better formulated as 18-electron, N,N-bonded, cis-dinitrogen dioxide (not hyponitrite) complexes in which there is a significant N-N interaction; thus, for example, $\text{IrP}_2(\text{NO})_2\text{Br}$ would become $\text{IrP}_2(\text{N}_2\text{O}_2)\text{Br}$. This alternate suggestion differs from the nitrene postulate¹ in that the N-N interaction is formed before rather than after oxygen abstraction. Dinitrogen dioxide intermediates, such as $\text{Ni}(\text{CO})_2(\text{N}_2\text{O}_2)$ and $\text{Co}(\text{en})_2(\text{N}_2\text{O}_2)^{2+}$, may also be involved in the conversion of $\text{Ni}(\text{CO})_4$ to $\text{Ni}(\text{NO})(\text{NO}_2)$ and *trans*- $\text{Co}(\text{en})_2(\text{NO})\text{Cl}^+$ to *cis*- $\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}^+$ by NO.¹⁹ Efforts to confirm such a scheme by isolating possible intermediates and by studying reaction 11 under varying conditions are continuing.

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(18) Reaction conditions: Initial absolute pressure was 2.99 atm (corrected for the vapor pressure of solvent, 2-butanone); temperature was 20° ; mole ratio of CO to NO was 1.1:2.0; 90 mg of Rh complex was used; $P_{\text{N}_2\text{O}} = P_{\text{CO}_2}$ within experimental error (3%); reactions were carried out in a closed stainless steel-glass reaction vessel. There was no reaction under identical conditions in the absence of the Rh complex.

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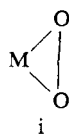
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SCF-X α Scattered Wave Calculation of the Electronic Structure of $\text{Pt}(\text{PH}_3)_2(\text{O}_2)$

Sir:

The metal-dioxygen bond in transition metal complexes containing chelated molecular oxygen (i) is



usually described qualitatively¹ as a combination of "forward donation" from filled O_2 $1\pi_u$ orbitals to

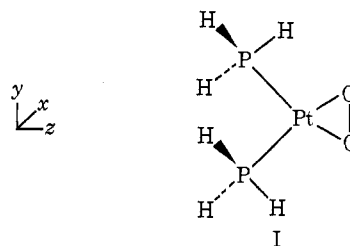
(1) F. R. Hartley, *Angew. Chem., Int. Ed. Engl.*, **11**, 596 (1972).

empty orbitals on the metal and "back-donation" from filled metal d orbitals to the half-filled O_2 $1\pi_g$ antibonding levels. Mason² notes that the resulting electronic configuration for O_2 approximates the first excited state of the free molecule, about one electron having been removed from the $1\pi_u$ orbitals (by forward donation) and added to the $1\pi_g$ orbitals (by back-donation). The O-O bond lengthening invariably observed upon chelation of dioxygen to a transition metal³ is explained as due to this replacement of bonding by antibonding electron density.

Dioxygen seems particularly suited among diatomic molecules to accept electrons from metals by π back-donation, since the half-filled character of its $1\pi_g$ orbitals brings them into the same energy range as filled metal d π orbitals, and d π - π_g overlap might therefore be efficient. This contrasts with such ligands as CO and ethylene, where the antibonding ligand π orbitals are empty. No quantitative calculations are available for metal-dioxygen complexes to aid in assessing the importance of back-donation therein. I report here such a study for dioxygenbis(phosphine)platinum, $\text{Pt}(\text{PH}_3)_2(\text{O}_2)$, an approximate model for the known compound $\text{Pt}(\text{PPh}_3)_2(\text{O}_2)$,⁴ which is a simple, stable dioxygen complex whose X-ray structure is established.⁵ The formally zerovalent platinum atom and relatively long O-O bond (1.51 Å; cf. 1.21 Å in free O_2) suggest that, if π back-donation is important in any dioxygen complex, it should be here.

The X α scattered-wave (X α SW) method, which has been thoroughly reviewed,⁶ was employed for this calculation. Briefly, it is a *first principles* self-consistent-field method which yields one-electron eigenvalues in excellent agreement with experiment, being equal or superior in this respect to the best *ab initio* calculations, but which requires only a small fraction of the computer time of even approximate Hartree-Fock treatments. The main applications of the X α SW method will probably be with large molecules, for which complete, accurate, and nonempirical calculations have previously been prohibitively expensive.

$\text{Pt}(\text{PH}_3)_2(\text{O}_2)$ was calculated in conformation I,



corresponding to the highest possible symmetry, C_{2v} . Dimensions were taken from the known structures of $\text{Pt}(\text{PPh}_3)_2(\text{O}_2)$ ⁵ and PH_3 .⁷ All valence and core levels

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(5) P. T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Can. J. Chem.*, **49**, 3772 (1971).

(6) (a) K. H. Johnson, *Advan. Quantum Chem.*, **7**, 143 (1973); (b) K. H. Johnson, J. G. Norman, Jr., and J. W. D. Connolly in "Computational Methods for Large Molecules and Localized States in Solids," F. Herman, A. D. McLean, and R. K. Nesbet, Ed., Plenum Press, New York, N. Y., 1972, pp 161-201; (c) J. C. Slater and K. H. Johnson, *Phys. Rev. B*, **5**, 844 (1972).

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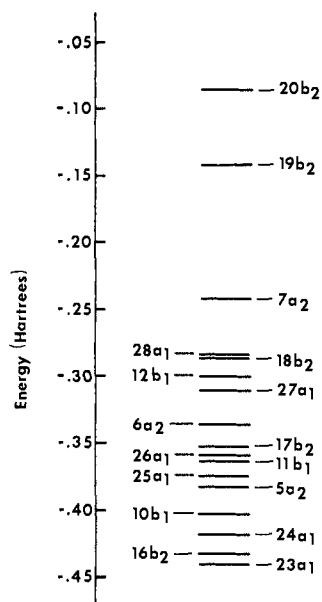


Figure 1. Upper portion of SCF-X α SW valence energy-level diagram for Pt(PH₃)₂(O₂). The highest occupied level is 7a₂.

were calculated explicitly in full self-consistent-field manner. The upper portion of the resulting valence energy-level diagram appears in Figure 1. The omitted lower portion contains only essentially unperturbed O₂ 2 σ_g and 2 σ_u and P 3s orbitals in the range -0.65 to -0.95 hartrees. Analysis of the character of each one-electron level yields the following conclusions.

(1) There are no levels involving significant mixing between Pt 5d and O₂ 1 π_g orbitals. Of the three levels with appreciable 1 π_g character, 18b₂ (an occupied level) is about 50% 1 π_g , 30% P 3p, and 15% Pt 6p_y; 7a₂ (the highest occupied level) is 100% 1 π_g , and 19b₂ (the lowest unoccupied level) is 50% 1 π_g and 50% Pt 6p_y. There are thus the equivalent of about three 1 π_g electrons in the molecule, but the only Pt orbital involved with the 1 π_g orbitals is 6p_y, empty in free Pt, and its involvement is large scale only in the lowest unoccupied molecular level. The Pt d orbitals of proper symmetry to overlap with 1 π_g are 5d_{xy} in a₂ and 5d_{yz} in b₂ symmetry. They are found instead to interact with P 3p_x (in 5a₂ and 6a₂) and 3s orbitals (16b₂) to form major components of the Pt-P bond.

(2) Pt-O₂ bonding is accomplished through extensive mixing of O₂ 1 π_u and 3 σ_g orbitals with Pt mainly 5d_{z²} and 5d_{x²-y²} orbitals in levels 23a₁, 24a₁, 25a₁, and 28a₁ and mixing of an O₂ 1 π_u with the Pt 5d_{z²} orbital in levels 10b₁ and 12b₁. The 3 σ_g appears comparable, not secondary, in importance to the 1 π_u orbital in the a₁ levels.

(3) Phosphorus 3d orbitals make up more than 6% of total phosphorus character only in 6a₂, where the figure is 17%. As a whole this level is 50% Pt 5d_{xy}, 30% P 3p_x, 3d_{z²}, and 3d_{yz}, and 20% H 1s. The 3d orbitals thus appear to hybridize with 3s and 3p functions in small amounts to promote better overlap, rather than serving in themselves as acceptor orbitals for "back-donation."

(4) Of the levels not mentioned above, all (26a₁, 11b₁, and 17b₂) have chiefly P-H character except 27a₁, mainly Pt 6s, and unoccupied 20b₂, mainly O₂ 3 σ_u .

The quantitative calculations thus appear to roughly

confirm Mason's picture of a shift in O-O bonding electrons toward the metal, through mixing of O₂ 1 π_u and 3 σ_g with Pt orbitals, and a buildup of extra antibonding electron density in the 1 π_g orbitals. However, the latter phenomenon apparently arises *not* through direct Pt d π \rightarrow O₂ 1 π_g back-donation but in some more subtle reorganization of electrons throughout the Pt, PH₃, and O₂ components as the molecule is formed. The exact nature of such reorganization should be sensitive to the particular ligand-metal combination bound to dioxygen, and indeed O-O distances in known complexes vary from 1.30 to 1.63 Å³—though I am not suggesting without further study that the picture developed here applies to all such complexes. It is not necessary to invoke d π \rightarrow π_g back-donation to explain the observed diamagnetism of Pt(PPh₃)₂(O₂), as compared to two unpaired electrons in free O₂. The presence of the platinum atom lifts the degeneracy of the O₂ 1 π_g orbitals, and distributes 1 π_g character among two fully occupied (18b₂ and 7a₂) levels and one unoccupied level (19b₂).

No experimental data are available for Pt(PPh₃)₂(O₂) to confirm these results. There is no reason to believe that the excellent agreement between experimental and X α SW-calculated one-electron energies observed in other cases, notably PtCl₄²⁻,⁸ PtCl₃(C₂H₄)⁻,⁹ and (C₅H₅)₂Fe,¹⁰ should not also be found here. Further calculations on metal-dioxygen complexes are planned, in particular on Pt(PF₃)₂(O₂). The present results will be presented in more detail when contour maps of electron density in important levels have been generated.

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Molecular Beam Chemistry. Facile Six-Center Reactions of Dimeric Chlorine with Bromine and with Hydrogen Iodide

Sir:

The formation of interhalogens by exchange reactions of diatomic molecules is known to proceed rapidly in both the gas phase and in solution.¹⁻⁴ Until recently, these processes were assumed to be elementary bimolecular reactions of the "four-center" type, AB + CD \rightarrow AD + BC. According to orbital symmetry arguments, such a reaction (nominally a 4n process) is

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