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ANALOGIES AMONG ACTIVE SITES OF COORDINATIVELY-UNSATURATED  
TRANSITION-METAL COMPLEXES, SURFACES, AND SUPPORTED CATALYSTS\*

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It has been shown by Ugo *et al.* [1] that the coordinatively-unsaturated transition-metal complex  $(PPh_3)_2Pt$  [bistriphenylphosphine-platinum(0)] exhibits a chemical reactivity and binding stability with respect to the molecules  $O_2$ ,  $CO$ ,  $SO_2$ ,  $C_2H_2$ ,  $C_2H_4$ ,  $H_2$ , and  $N_2$  which can be compared on a one-to-one basis with those of a chemisorption site on a platinum surface. Such analogies have also been made for coordinatively-unsaturated complexes of other transition metals, such as iridium and rhodium [2,3]. In this communication, we suggest that the strong similarity between the reactivity of coordinatively-unsaturated transition-metal complexes and the catalytic activity of transition-metal surfaces, including supported catalysts, is probably not fortuitous and can be understood in terms of the similarity of local electronic structures.

Electronic structures of transition-metal complexes of the type  $L_2M$ ,  $L_2MH_2$ , and  $L_2MC_2H_2$  ( $M = Pt, Ir$ ), in which the triphenylphosphine ligands ( $L = PPh_3$ ) have been modeled by electronically similar but simpler phosphine ligands ( $L = PH_3$ ), have been calculated by the self-consistent-field X-alpha scattered-wave (SCF-X $\alpha$ -SW) molecular-orbital method [4].

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\*Research sponsored by the Office of Naval Research, the National Science Foundation, Grant Nos. <sup>NISF-</sup>DMR74-15224 and DMR76-80895 (through the Center for Materials Science and Engineering), and by the Donors of the Petroleum Research Fund administered by the American Chemical Society.

Similar SCF-X $\alpha$ -SW studies of  $(\text{PH}_3)_2\text{PtO}_2$  and  $(\text{PH}_3)_2\text{PtC}_2\text{H}_4$  have previously been reported by Norman [5] and the results successfully used to explain the photoelectron spectra and homogeneous catalytic activity of these complexes.

The resulting electronic structure of a coordinatively-unsaturated transition-metal complex of the type  $\text{L}_2\text{M}$ , shown schematically in Fig. 1(a), is characterized by a strong covalent interaction between the ligand ( $\text{L} = \text{PH}_3$ ) lone-pair p-like orbitals and the metal ( $\text{M} = \text{Pt}, \text{Ir}, \text{etc.}$ ) d orbitals along the metal-ligand direction (the yz direction for the coordinate system shown). The antibonding component of this interaction pushes the  $\text{M}(\text{d}_{yz}^*)$  orbital, the highest occupied molecular orbital (HOMO) shown in Fig. 1(a), significantly closer in energy (as compared with the nonbonding  $\text{d}_{xy}$ ,  $\text{d}_{xz}$ , and  $\text{d}_{x^2-y^2}$  orbitals) to the lowest unoccupied molecular orbitals (LUMO), e.g., the antibonding  $\sigma_u$  and  $\pi^*$  LUMO of  $\text{H}_2$  and  $\text{C}_2\text{H}_2$ , respectively, illustrated in Figs. 1(d) and (e). This facilitates overlap of these symmetry-conserving orbitals [6] and reduces the activation energy for electron flow between HOMO and LUMO, thereby promoting the formation of dihydride complexes of the type  $\text{L}_2\text{MH}_2$  and acetylene complexes of the type  $\text{L}_2\text{MC}_2\text{H}_2$ . The detailed electronic structures of the latter complexes are described elsewhere [7]. These results are consistent with the orbital mechanism for metal-catalyzed  $\text{H}_2$  bond cleavage and metal-dihydride bond formation suggested by Vaska and Werneke [3] and represented schematically in Fig. 2. Since a deuterium molecule ( $\text{D}_2$ ) is orbitally similar to the hydrogen molecule ( $\text{H}_2$ ), the same mechanism is applicable to  $\text{D}_2$  bond cleavage suggesting how a coordinatively-unsaturated transition-metal site catalyze  $\text{H}_2$ - $\text{D}_2$  exchange.

In order to elucidate the relationship between the electronic structure

of a coordinatively-unsaturated transition-metal complex of the type  $L_2M$  and that of an active site on a transition-metal surface, we substitute successively larger groups of transition-metal atoms ( $M_x$ ;  $x = 1, 2, 3, \dots, n$ ) for the phosphine ligands (L). The electronic structure of the resulting aggregate, as determined by the SCF- $X\alpha$ -SW method, expands to the manifold of bonding, nonbonding, and antibonding d-orbital eigenstates (the "d band") characteristic of a transition-metal (e.g., platinum) cluster [8,9], shown schematically in Fig. 1(c). As described in Ref. 8, this manifold, by virtue of the component orbital symmetries and charge distributions, can be partitioned into eigenstates that are delocalized throughout the cluster (the "bulk-like" states) and eigenstates that are primarily localized at the coordinatively-unsaturated atomic sites on the cluster periphery (the "surface-like" states). Such clusters can therefore be used as models for the bulk and surface electronic structures of the corresponding crystalline metals, as well as models for small metal particles of catalytic importance [8,9]. Recent SCF- $X\alpha$ -SW studies by Messmer and Salahub [10] confirm that even for aluminum, a highly delocalized nearly-free-electron-like metal that has been described traditionally in terms of the  $\vec{k}$ -space band-structure representation of solid-state physics, relatively small clusters are sufficient to provide an accurate "real-space" representation of bulk and surface electronic structure, including chemisorption.

The above-mentioned partitioning of the eigenstates of a transition-metal cluster into "bulk" and "surface" components is reproduced schematically in Fig. 1(c). In close analogy to the electronic structure of a coordinatively-unsaturated transition-metal complex shown in Fig. 1(a), in which a  $d_{yz}^*$  orbital is split off in energy from the nonbonding d orbitals by the strong antibonding interaction with the ligand p-like lone-pair orbitals, the direct interaction of the d orbitals of a metal site on the cluster periphery

with the d orbitals on neighboring metal sites (viewed as "ligands") leads to a splitting off in energy of a strongly antibonding  $d_{yz}^*$  orbital from the top of the main d-orbital manifold. For cluster geometries other than the one implied in Fig. 1(c), the most strongly antibonding orbital can have a different local symmetry, e.g.,  $d_{z^2}^*$  [7], and it is likely that for more general cluster configurations or surface morphologies a range of orbital symmetries will be encountered. Such orbitals can be interpreted as cluster analogues of "surface states" that are split off in energy from the top of the d band of a bulk crystalline transition metal, e.g., the surface states recently observed experimentally and calculated via Green's function theory by Weng *et al.* [11]. As in Fig. 1(a), the  $d_{yz}^*$  orbital shown in Fig. 1(c) is symmetry-conserving [6] with respect to the LUMO of reactant molecules such as  $H_2$  and  $C_2H_2$  shown in Fig. 1(a) and, when occupied, suggests a mechanism of  $H_2$  bond cleavage at a single transition-metal site on a cluster or surface analogous to that shown for a coordinatively-unsaturated metal site in Fig. 2. This mechanism and the concomitant involvement of metal d orbitals in metal-hydride bond formation (cf. Ref. 9) are fundamentally different from theoretical models for dissociative hydrogen chemisorption on transition metals proposed by other workers [12,13]. However, the mechanism of  $H_2$  bond cleavage shown in Fig. 2, in conjunction with the theoretical model for the bonding of dissociated hydrogen atoms to a platinum cluster presented in Ref. 9, is consistent with the empirical model for dissociative  $H_2$  chemisorption on platinum surfaces recently suggested by Christmann and Ertl [14].

As a final example of the analogy between coordinatively-unsaturated transition-metal complexes and active surface sites, we consider the electronic structure of transition-metal atoms dispersed on a silica ( $SiO_2$ ) substrate, a prototype model for a silica-supported metal catalyst. Recent extended

X-ray absorption fine structure (EXAFS) studies of such systems suggest that there are significant catalyst-support interactions [15]. Previous theoretical studies have shown that one can effectively model the electronic structure of  $\text{SiO}_2$  by performing SCF- $X\alpha$ -SW molecular-orbital calculations on representative clusters [16]. The results of these calculations are in good quantitative agreement with the measured electronic band structure of silica, including the valence band density of states, as determined by photoelectron and X-ray spectroscopies, and the energy gap between valence and conduction bands, as determined by optical spectroscopy [16]. Using the same theoretical approach, we have constructed theoretical models for platinum and ruthenium atoms supported on  $\text{SiO}_2$ . Although definitive structural data are not yet available, a possible metal-support configuration, consistent with EXAFS data [15], is the one illustrated schematically in Fig. 1(b), in which the oxygen atoms at the  $\text{SiO}_2$ -M interface serve as "ligands" of the metal atom in a fashion analogous to the coordinatively-unsaturated  $L_2M$  complex considered in Fig. 1(a).

The primarily covalent interaction between the metal d orbitals and oxygen nonbonding 2p orbitals that constitute the top portion of the  $\text{SiO}_2$  valence band lead to metal-oxygen bonding orbitals embedded in the valence band and to nonbonding and antibonding d orbitals split off in energy from the top of the valence band and positioned within the  $\text{SiO}_2$  band gap like "deep-level" transition-metal impurity states in the band gap of a semiconductor [17]. The highest of these antibonding orbitals is principally metal  $d_{yz}$  in character for the chosen coordinate system and has a one-to-one correspondence with the HOMO of the coordinatively-unsaturated  $L_2M$  ( $M = \text{Pt}$ ) complex [cf. Fig. 1(a)] which has been argued to be responsible for activation of  $\text{H}_2$  dissociation through symmetry-conserving overlap with the  $\text{H}_2$   $\sigma_u$  orbital. The orbital symmetries and orderings are qualitatively similar for  $\text{SiO}_2\text{Pt}$

and  $\text{SiO}_2\text{Ru}$ , although in the latter system the  $d_{yz}^*$  antibonding orbital is empty. This difference in orbital occupancy suggests that the bonding and catalytic activity of Ru atoms on silica should be significantly different from those of Pt atoms on silica. In support of this result are recent EXAFS, electron microscopy, and chemisorption studies [15,18] which indicate that ruthenium interacts strongly with a silica substrate, forms "raft-like" structures, and chemisorbs oxygen ( $\text{O}_2$ ) molecularly, whereas silica-supported platinum tends not to form rafts and chemisorbs  $\text{O}_2$  dissociatively. SCF- $\text{X}\alpha$ -SW cluster models for ruthenium aggregates on  $\text{SiO}_2$  [19] suggest that the  $\text{SiO}_2$ -Ru bonding perpendicular to the silica surface actually enhances Ru-Ru bonding parallel to the surface, thereby providing a theoretical justification for the formation of raft-like structures.

#### References

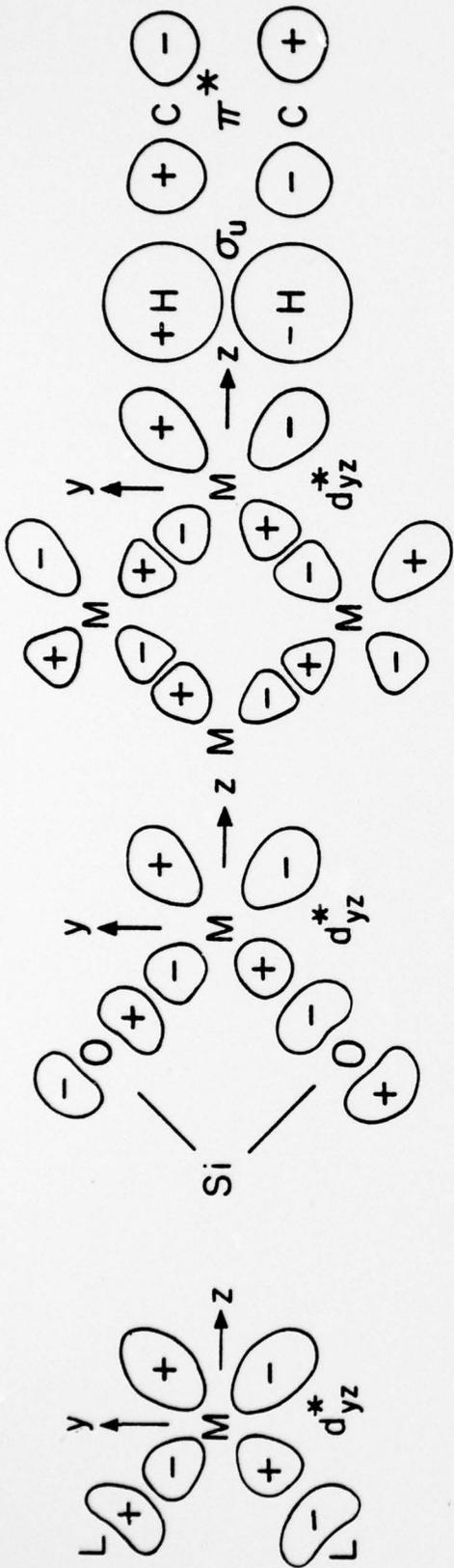
- [1] R. Ugo, G. LaMonica, F. Cariati, S. Cenini, and F. Conti, *Inorg. Chim. Acta* 4 (1970) 390.
- [2] R. Ugo, *Catal. Rev.-Sci. Eng.* 11 (1975) 225.
- [3] L. Vaska and M. F. Werneke, *Trans. N. Y. Acad. Sci.* 31 (1971) 70; G. G. Eberhardt and L. Vaska, *J. Catal.* 8 (1967) 183.
- [4] J. C. Slater and K. H. Johnson, *Phys. Rev.* B5 (1972) 844; K. H. Johnson, in: *Advances in Quantum Chemistry*, Vol. 7, Ed. P.-O. Löwdin (Academic, New York, 1973) p. 143; J. C. Slater, *The Self Consistent Field for Molecules and Solids*, Vol. 4 of *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974) p. 101; K. H. Johnson, in: *Annual Review of Physical Chemistry*, Vol. 26, Eds. H. Eyring, C. J. Christensen, and H. S. Johnston (Annual Reviews, Palo Alto, 1975) p. 39.
- [5] J. G. Norman, Jr., *Inorg. Chem.* 16 (1977) 1328.

- [6] R. G. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry* (Academic, New York, 1969).
- [7] A. C. Balazs, S.M. Thesis, Department of Materials Science and Engineering, June, 1977; A. C. Balazs and K. H. Johnson (manuscript in preparation); K. H. Johnson, in Proceedings of the Third International Summer Institute in Surface Science, *Crit. Rev. Solid State Sci.* (in press); K. H. Johnson, *Int. J. Quantum Chem.* 11S (1977) 39.
- [8] R. P. Messmer, S. K. Knudson, K. H. Johnson, J. B. Diamond, and C. Y. Yang, *Phys. Rev.* B13 (1976) 1396.
- [9] R. P. Messmer, D. R. Salahub, K. H. Johnson, and C. Y. Yang, *Chem. Phys. Lett.* 51 (1977) 84.
- [10] R. P. Messmer and D. R. Salahub, *Chem. Phys. Lett.* 49 (1977) 59; D. R. Salahub and R. P. Messmer, *Phys. Rev.* B16 (1977) 2526; R. P. Messmer and D. R. Salahub, *Phys. Rev.* B16 (1977) 3415.
- [11] S. L. Weng, *J. Vac. Sci. Techn.* (in press); S. L. Weng, T. Gustafson, and E. W. Plummer, *Phys. Rev. Lett.* 39 (1977) 822; S. L. Weng, *Phys. Rev. Lett.* 38 (1977) 434.
- [12] C. F. Melius, *Chem. Phys. Lett.* 39 (1976) 287; C. F. Melius, J. W. Moskowitz, A. P. Mortola, M. B. Baille, and M. A. Ratner, *Surface Sci.* 59 (1976) 279.
- [13] A. B. Kunz, M. P. Guse, and R. J. Blint, *J. Phys.* B8 (1975) L358; R. J. Blint, A. B. Kunz, and M. P. Guse, *Chem. Phys. Lett.* 36 (1975) 191; A. B. Kunz, M. P. Guse, and R. J. Blint, in: *Electrocatalysis of Non-Metallic Surfaces*, Ed. A. D. Franklin (National Bureau of Standards, Spec. Publ. 455, Washington, D. C., 1976) p. 53.
- [14] K. Christmann and G. Ertl, *Surface Sci.* 60 (1976) 365.

- [15] J. H. Sinfelt and F. W. Lytle (to be published and private communication).
- [16] J. A. Tossell, D. J. Vaughan, and K. H. Johnson, Chem. Phys. Lett. 20 (1973) 329; J. A. Tossell, J. Am. Chem. Soc. 97 (1975) 4840; J. A. Tossell, J. Phys. Chem. Solids 36 (1975) 1723.
- [17] L. A. Hemstreet, Phys. Rev. B15 (1977) 834.
- [18] J. H. Sinfelt (to be published and private communication).
- [19] H. J. Kolari and K. H. Johnson (to be published).

Figure Captions

- Figure 1. Comparison of the electronic structures associated with coordinatively-unsaturated transition-metal (e.g.,  $M = Pt$ ) sites: (a) in a transition-metal coordination complex ( $L = PH_3$ ); (b) on a silica ( $SiO_2$ ) support; (c) at the periphery or "surface" of a transition-metal cluster. Also shown, for comparison, are the HOMO and LUMO of the reactant molecules: (d)  $H_2$  and (e)  $C_2H_2$ . All the orbital energy levels shown in the lower half of the diagram are displayed schematically on the same relative scale and for  $M = Pt$  in (a), (b), and (c) span an energy range of approximately 0.5 Ry. Symmetry-conserving orbital wavefunctions involved in reactivity are mapped in the y-z plane in the upper half of the diagram.
- Figure 2. Proposed orbital mechanism for  $H_2$  dissociation at a coordinatively-unsaturated transition-metal site (adapted from Ref. 3).



L L<sub>2</sub>M M

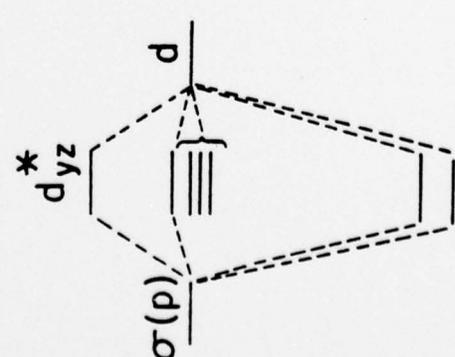
SiO<sub>2</sub>

SiO<sub>2</sub>M M

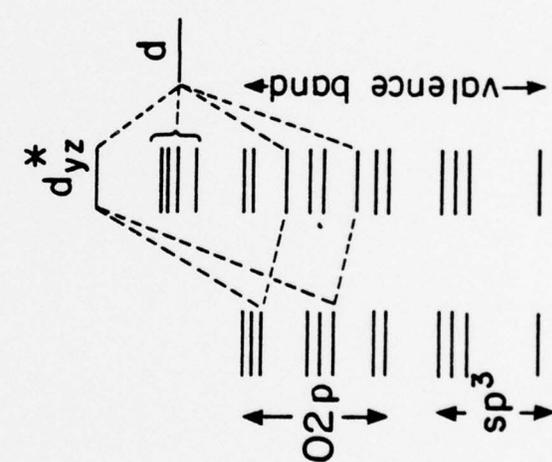
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H<sub>2</sub>  $\sigma_u$

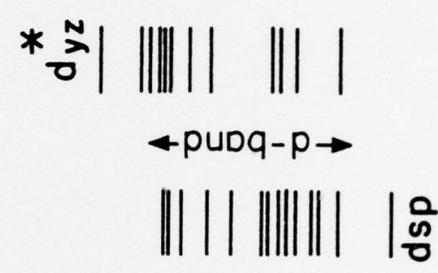
C<sub>2</sub>H<sub>2</sub>  $\pi^*$



(a)



(b)



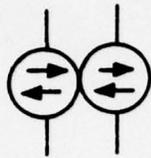
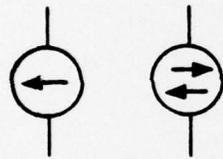
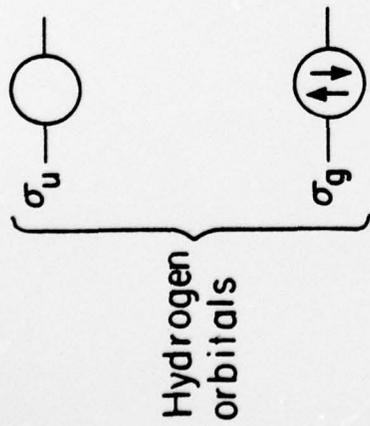
(c)

$\sigma_g$

(d)

$\pi$

(e)



Hydrogen species

