

Preliminary communication

THE PROTON AS A PROBE OF CLUSTER BONDING. THE UV PHOTOELECTRON SPECTRA OF TWO HYDRIDO TRANSITION METAL CLUSTERS

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Summary

A direct comparison of the gas phase UV photoelectron spectra of the iso-electronic pairs $\text{Mn}_3(\mu_2\text{-H})_3(\text{CO})_{12}/\text{Fe}_3(\text{CO})_{12}$ and $\text{Fe}_3(\mu_2\text{-H})_3(\text{CO})_9(\mu_3\text{-CCH}_3)/\text{Co}_3(\text{CO})_9(\mu_3\text{-CCH}_3)$ in conjunction with those of appropriate model compounds demonstrates substantial stabilization of selected metal orbitals on addition of edge-bridging protons, locates the metal-metal ionizations in the complex *d* band of the unbridged cluster and illustrates a significant difference between the ionization behavior of first and third row transition metal clusters.

As evidenced by recent reviews [1,2], the spatial location of the proton in hydrido transition metal cluster complexes has revealed significant information on the nature of the metal-metal interactions. Recent work also demonstrates that the introduction of a proton into or the deletion of a proton from a metal-metal bonded system can have dramatic chemical effects [3,4]. As both geometry and chemistry ultimately reflect the distribution of valence electron density, the effect of the proton on electron density will also be revealed by the spectroscopic properties of hydrido metal clusters. One spectroscopic probe of electronic structure is UV photoelectron spectroscopy (PES) and an effective empirical use of this technique is the direct comparison of the PES of isoelectronic molecules that differ only in the replacement of a nucleus of atomic number *z* by one of *z*-1 plus a proton. See for example the comparisons HBS/CS and $\text{B}_2\text{H}_6/\text{C}_2\text{H}_4$ [5]. We have recently isolated and characterized the new compound $\text{Fe}_3(\mu_2\text{-H})_3(\text{CO})_9(\mu_3\text{-CCH}_3)$ (I) and have demonstrated by means of an X-ray diffraction study that the structure of this compound is analogous to that of the isoelectronic $\text{Co}_3(\text{CO})_9(\mu_3\text{-CCH}_3)$ (II) except that the edges of the metal triangle are bridged by hydrogens [6]. Comparison of the PES of these two compounds as well as those of $\text{Mn}_3(\mu_2\text{-H})_3(\text{CO})_{12}$ (III)

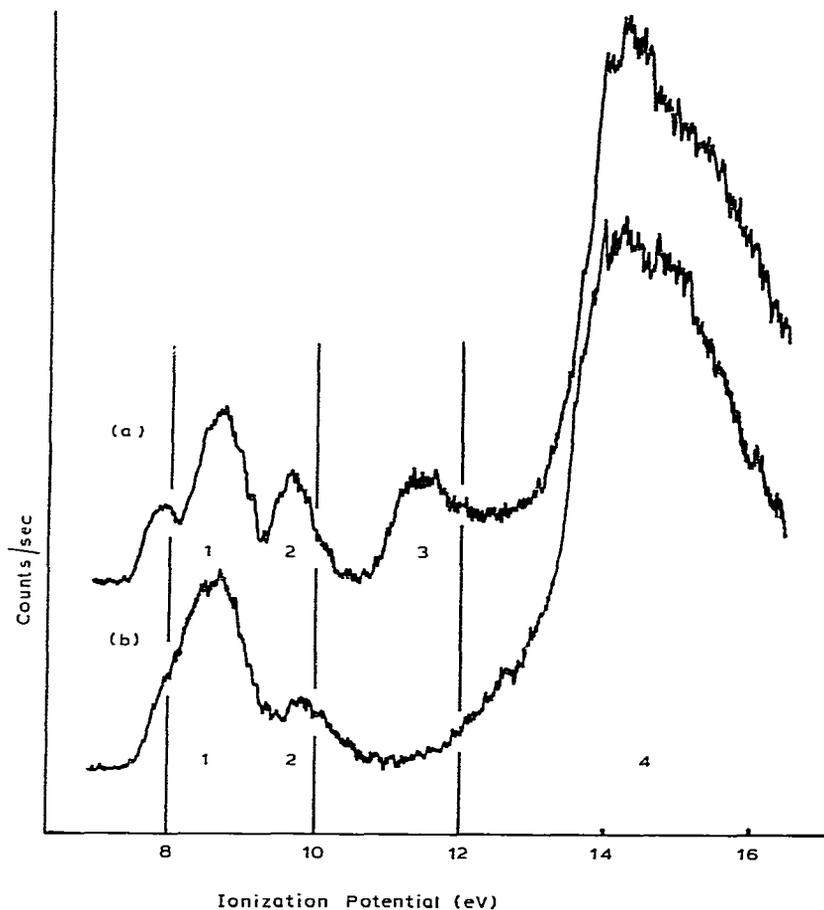


Fig. 1. The He(I) gas phase photoelectron spectra of (a) $\text{Fe}_3(\mu_2\text{-H})_3(\text{CO})_9(\mu_3\text{-CCH}_3)$ and (b) $\text{Co}_3(\text{CO})_9(\mu_3\text{-CCH}_3)$.

it is clear that the intensity losses in both cases are associated with the M—M ionizations of II and IV. However, the M—M IP's themselves cannot be established unless the extent of the change in the "lone pair" IP's on changing the nuclear charge of the metal atoms can be estimated. In fact the PES of three isoelectronic series ($\text{Ni}(\text{CO})_4$, $\text{Co}(\text{CO})_3\text{NO}$, $\text{Fe}(\text{CO})_2(\text{NO})_2$ [13], $\text{Ni}(\text{CO})_4$, $\text{HCo}(\text{CO})_4$ [14], and $\text{S}_2\text{Fe}_2(\text{CO})_6$, $\text{H}_2\text{C}_2\text{Co}_2(\text{CO})_6$ [15,16]) demonstrate that the "lone pair" IP's of first row transition metals only change 0.1 to 0.3 eV for a change in nuclear charge of 1. A corroborating observation is that in the PES of I and II band 2 only shifts about 0.1 eV to lower IP in going from Co to Fe and in the PES of III and IV band 1b only shifts 0.3 eV to lower IP in going from Fe to Mn. Because of the relative insensitivity of the "lone pair" bands to nuclear charge. The difference in the 3d bands with and without bridging protons yields the approximate M—M IP's at 8.3 eV in II and 7.8 eV in IV. Thus, in I, II, and III the lowest IP is that of a "lone pair" orbital*.

*The fact that band 1 of I is split into two components indicates that strict partitioning into "lone pairs" and MM bonding orbitals is, not surprisingly, an over simplification.

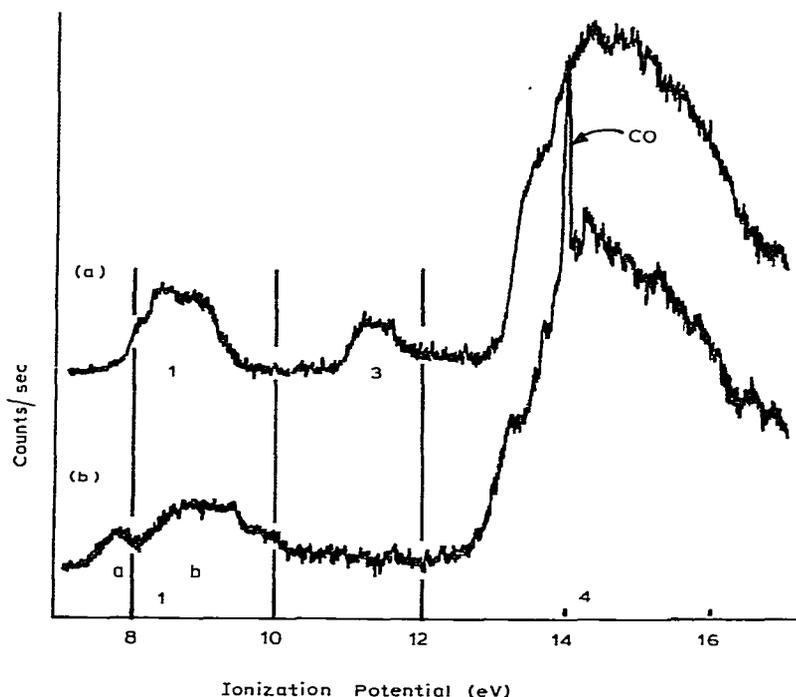


Fig. 2. The He(I) gas phase photoelectron spectra of (a) $\text{Mn}_3(\mu_2\text{-H})_3(\text{CO})_{12}$ and (b) $\text{Fe}_3(\text{CO})_{12}$.

The insensitivity of the $3d$ bands of I and II to nuclear charge serves to point out a significant difference between first row and third row transition metal systems. The $3d$ orbital energy depends strongly upon nuclear charge but the IP of a $3d$ electron need not. As pointed out by Calabro and Lichtenberger, this is quite clear for atoms [17]. Because there are fewer electrons in the ion than atom, electrons in orbitals of the same or greater radii experience decreasing shielding of the nucleus. The additional resulting stabilization, called relaxation energy, causes the ionization energy to be less than the negative of the orbital energy. The "lone pair" ionizations of transition metal compounds, particularly organometallic compounds, exhibit large relaxation energies relative to other ionizations. This not only has a critical role in understanding the placement of the "lone pair" ionizations with respect to other ionizations, but also modulates the effect of nuclear charge on the "lone pair" ionization energies. As the relaxation energy for first row transition metals increases an estimated 0.4 eV for an increase in z of 1 [18], the effect of increased nuclear charge in going from Mn to Fe to Co is significantly offset by the increase in relaxation energy. In fact, the observations show that if the number, type and arrangement of ligands are approximately the same, all but about 0.2 eV of the increase in IP caused by the greater nuclear charge is cancelled by the increase in relaxation energy. This is to be contrasted with the behavior of $\text{Os}_3(\text{CO})_{12}$ and $\text{Re}_3(\text{CO})_{12}\text{H}_3$ in which both $5d$ "lone pair" bands in the PES decrease significantly (0.8 eV) in going from Os to Re [11]. As the relaxation energy decreases in going down a group [17] the "lone pair" ionizations for the third row compounds appear at higher ionization

energy and are well separated from the M—M ionizations, i.e., for $\text{Fe}_3(\text{CO})_{12}$ the “lone pair” ionizations are about 1 eV lower than for $\text{Os}_3(\text{CO})_{12}$. Likewise effect of nuclear charge on “lone pair” ionization energy is stronger for third row atoms as the average change in relaxation energy per nuclear charge change of 1 is estimated to be less than that for first row atoms [17]. Just as the higher IP's of third row transition metals relative to first row are reflected in their chemistry [19] so too, one expects significant differences in the chemistry of analogous first and third row clusters especially in terms of the relative ease of oxidative cleavage of the metal—metal bonds vs. formation of higher cluster oxidations states.

A complete account of these and related experiments will be forthcoming.

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