Journal of Organometallic Chemistry, 215 (1981) C48-C52 Elsevier Sequoia S.A., Lausanne - Printed in The Netherlands

Preliminary communication

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

KWAI S. WONG, TAMAL K. DUTTA and THOMAS P. FEHLNER^{*} Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556 (U.S.A.) (Received March 6th, 1981)

Summary

A direct comparison of the gas phase UV photoelectron spectra of the isoelectronic pairs $Mn_3(\mu_2-H)_3(CO)_{12}/Fe_3(CO)_{12}$ and $Fe_3(\mu_2-H)_3(CO)_9(\mu_3-CCH_3)/CO_3(CO)_9(\mu_3-CCH_3)$ 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 B_2H_6/C_2H_4 [5]. We have recently isolated and characterized the new compound $Fe_3(\mu_2-H)_3(CO)_9(\mu_3-CCH_3)$ (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 $Co_3(CO)_9(\mu_3-CCH_3)$ (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 $Mn_3(\mu_2-H)_3(CO)_{12}$ (III)



and $Fe_3(CO)_{12}$ (IV) reveals (a) a substantial increase in selected metal IP's on the introduction of edge-bridging protons, (b) the location of the IP's associated with the metal—metal bonds in II and IV and (c) a significant difference between the ionization behavior of first and third row transition metal clusters.

The PES of I and II (Fig. 1) are assigned using $Co_4(CO)_{12}$ as a model compound [7]*. Band 1 of II contains the three Co 3d ionizations associated with the Co–Co bonds as well as the nine Co 3d lone pair (" t_{2e} ") ionizations; band 2 results from ionization of the degenerate pair of orbitals involved in the interactions of the apical carbon and the metal triangle, and band 4 includes the former 5 σ and π ionizations of the CO ligands. This assignment is consistent with that already reported [8] as well as with qualitative MO calculations [9]. In going from II to I relative intensity is lost from band 1 and a roughly equivalent intensity appears as band 3 at 11.5 eV. Band 3 gains relative intensity on using a lower photon energy (Ne(I)) and thus, is due to ionizations with significant H 1s character [10], i.e., the Fe–H–Fe ionizations. Characteristic M-H-M IP's were first observed in a comparison of PES of $\operatorname{Re}_3(\mu_2-H)_3(CO)_{12}$ and $\operatorname{Os}_3(CO)_{12}$ [11] and are consistent with the PES of mononuclear hydrido metal carbonyls as well [12]. The PES of III and IV (Fig. 2) are assigned in the manner previously reported for the third row analogs with band 3 in III assigned to the Mn-H-Mn IP's [11].

The quantitative changes in the lowest IP bands in going from II to I and from IV to III yields further information. After matching the intensities of bands 4, a direct difference of the spectra shows the missing intensity in band 1 of I is centered at 8.3 eV. A similar comparison of the spectra of III and IV shows that band 1a at 7.8 eV in IV is missing in III. As bridging protons stabilize the orbitals with significant amplitudes between the metal atoms,

^{*}The vaporization behavior of all materials has been characterized by temperature programmed mass spectrometry.



Fig. 1. The He(I) gas phase photoelectron spectra of (a) $Fe_3(\mu_2-H)_3(CO)_9(\mu_3-CCH_3)$ and (b) $Co_3(CO)_9(\mu_3-CCH_3)$.

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 (Ni(CO)₄, Co(CO)₃NO, Fe(CO)₂(NO)₂ [13], Ni(CO)₄, HCo(CO)₄ [14], and S₂Fe₂(CO)₆, H₂C₂Co₂(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 o.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 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) Mn₃ (μ_2 -H)₃ (CO)₁₂ and (b) Fe₃ (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 $Os_3(CO)_{12}$ and $Re_3(CO)_{12}H_3$ 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 $Fe_3(CO)_{12}$ the "lone pair" ionizations are about 1 eV lower than for $Os_3(CO)_{12}$. 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.

Acknowledgments. The support of the National Science Foundation under Grant CHE 79-15220 is gratefully acknowledged.

References

- 1 R. Bau, R.G. Teller, S.W. Kirtley and R.F. Koetzle, Accounts Chem. Res., 12 (1979) 176.
- 2 A.P. Humphries and H.D. Kaesz, Prog. Inorg. Chem., 25 (1979) 145.
- 3 W.A. Herrmann, J. Plank, D. Riedel, M.L. Ziegler, K. Weidenhammer, E. Goggloz and B. Balbach, J. Amer. Chem. Soc., 103 (1981) 63.
- 4 K.E. Inkrott and S.G. Shore, Inorg. Chem., 10 (1979) 2817.
- 5 T.P. Fehlner and D.W. Turner, J. Amer. Chem. Soc., 95 (1973) 7175; C.R. Brundle, M.B. Robin, H. Basch, M. Pinsky and A. Bond, J. Amer. Chem. Soc., 92 (1970) 3863.
- 6 K.S. Wong and T.P. Fehlner, J. Amer. Chem. Soc., 103 (1981) 966.
- 7 T.P. Fehlner, unpublished data.
- P. Chesky and M.B. Hall, Abstr. 2nd Chem. Congress of N. Amer. Continent, Las Vegas, 1980 INORG 175. G. Granozzi, S. Agnolin and M. Casarin, J. Organometal. Chem., 208 (1981) C6.
 J. Evans, J. Chem. Soc. Dalton, (1980) 1005; B.E.R. Schilling and R. Hoffmann, J. Amer. Chem.
- Soc., 101 (1979) 3456.
- 10 J.W. Rabalais, Principles of Ultraviolet Photoelectron Spectroscopy, Wiley-Interscience, New York, 1977.
- 11 J.D. Green, D.M.P. Mingos and E.A. Seddon, J. Organometal. Chem., 185 (1980) C20.
- 12 M.F. Guest, B.R. Higginson, D.R. Lloyd and I.H. Hillier, J. Chem. Soc. Faraday II, 71 (1975) 902.
- 13 I.H. Hillier, M.F. Guest, B.R. Higginson and D.R. Lloyd, Mol. Phys., 27 (1974) 215.
- 14 S. Cradock, E.A.V. Ebsworth and A. Robertson, J. Chem. Soc. Dalton, (1973) 22.
- E.L. Anderson, T.P. Fehlner, A.E. Foti and D.R. Salahub, J. Amer. Chem. Soc., 102 (1980) 7422;
 H. Van Dam, J.N. Louwen, A. Oskam, M. Doran and I.H. Hillier, J. Electron Spectr. Rel. Phen., 21 (1980) 57.
- H. Van Dam, D.J. Stufkens, A. Oskam, M. Doran and I.H. Hillier, J. Electron Spectr. Rel. Phen., 21 (1980) 47; R.L. DeKock, T.V. Lubben, J. Hwang and T.P. Fehlner, Inorg. Chem., 20 (1981) 1627.
- 17 D.D. Calabro and D.L. Lichtenberger, Inorg. Chem., 19 (1980) 1732.
- 18 D.L. Lichtenberger, private communication.
- 19 J.E. Huheey, Inorganic Chemistry; Principles of Structure and Reactivity, Harper & Row, New York, 2nd Ed., 1978, p. 728.