Inorg. Chem. **1981**, *20*, 1327-1328 **1327**

Contribution from the Departments of Chemistry,
Auburn University, Auburn, Alabama 36849,
and The University of Louisville, Louisville, Kentucky 40292

Electronic Structures of Some η^3-Allyl Transition-Metal Complexes

S. D. Worley,*[1a] Dorothy H. Gibson,*[1b] and Wen-Liang Hsu[1b]

Received July 31, 1980

In recent years there has been much interest in the electronic structures of transition-metal carbonyl π complexes of hydrocarbons in these laboratories[2-5] and in others.[6] A primary thrust of the work in these laboratories has been to demonstrate that the ultraviolet photoelectron spectra (UPS) of the stable complexes of intriguing labile transients such as cyclobutadiene can be used in estimating the π ionization energies of the transient.[2,3] In fact, recent UPS studies by Heilbronner and co-workers[7] on tetra-*tert*-butylcyclobutadiene have supported our predictions for the π electronic structure of the parent cyclobutadiene. This note will address UPS of several transition-metal complexes of and the electronic structure of another interesting transient species—the allyl radical.

Results and Discussion

The low-ionization-energy regions of the photoelectron spectra of four η^3-allyl transition-metal carbonyl complexes are shown in Figure 1. The resolution in the region above 12 eV for these spectra was not sufficient to render definitive assignments for the ionization bands corresponding to removal of electrons from σ-bonding orbitals. However, assignment of the bands in the region below 12 eV for these complexes would appear to be straightforward.

The spectrum of η^3-allylmanganese tetracarbonyl, A, exhibits four resolved band components below 12 eV. The I_1 and I_2 components at 8.05 and 8.48 eV, respectively, must correspond to ionization of orbitals primarily confined to the transition metal Mn; ample precedent for such an assignment exists in the literature.[2-6] Thus, the I_3 and I_4 components at 9.03 and 11.13 eV can be assigned to ionization of the perturbed π orbitals on the allyl ligand. Using a very elaborate photoelectron spectrometer, Houle and Beauchamp were able to obtain the spectrum of the allyl radical.[8] They report a first ionization potential of 8.13 eV for this radical which, of course, must refer to ionization of the highest occupied π orbital which is primarily nonbonding in character. Thus, it is evident that this π orbital is perturbed significantly (stabilized by ca. 0.9 eV) by the bonding interaction with the manganese tetracarbonyl moiety. In fact, the 0.9-eV perturbation is almost exactly the same as that (0.89 ± 0.07 eV)[2,3] observed for the highest occupied π orbital of a number of hydrocarbons when these systems are coordinated to an iron tricarbonyl moiety. While this may seem fortuitous, a similar observation has been reported for the molybdenum, chromium, and iron carbonyl complexes of norbornadiene.[5] It is interesting that such a divergent series of transition-metal carbonyl complexes has similar perturbation energy for the π HOMO; however, there would seem to be no theoretical justification for this experimental observation. Because of overlapping bands due to decomposition products of 3-butenyl nitrite used to generate the allyl radical, Houle and Beauchamp were not able to locate higher ionization bands for the transient radical.[8] In any case the I_2 process for the allyl radical would be subject to the complication introduced by multiplet splitting (cf. trimethylenemethane[9]) such that little useful comparison with I_4 for complex A could be accomplished.

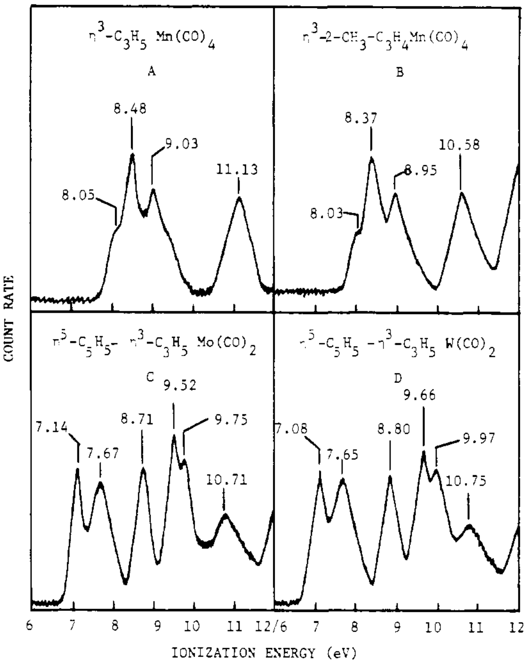

Figure 1. Photoelectron spectra of some η^3-allyl transition-metal complexes. The excitation source was the He I resonance line.

The appearance of the photoelectron spectrum of (η^3-2-methallyl)manganese tetracarbonyl, B, is very similar to that for A, as would be expected. Again I_1 and I_2 at 8.03 and 8.37 eV can be assigned to ionization of orbitals confined primarily to Mn, while I_3 and I_4 at 8.95 and 10.58 eV must refer to ionization of the perturbed allyl π orbitals. It should be noted that introduction of the methyl group at the 2 position on allyl causes greater destabilization of the second π orbital (0.55 eV) than of the HOMO (0.08 eV). This observation is entirely in accord with simple MO arguments in that the HOMO for the allyl radical contains a node at position 2, while the second π orbital contains maximum orbital density at this position. Such effects have been observed previously in the UPS of substituted unsaturated hydrocarbons.[10]

---

(1) (a) Auburn University. (b) The University of Louisville

(2) Worley, S. D.; Webb, T. R.; Gibson, D. H.; Ong, T. S. *J. Organomet. Chem.* **1979**, *168*, C16.

(3) Worley, S. D.; Webb, T. R.; Gibson, D. H.; Ong, T. S. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 189.

(4) Hill, W. E.; Ward, C. H.; Webb, T. R.; Worley, S. D. *Inorg. Chem.* **1979**, *18*, 2029.

(5) Worley, S. D.; Webb, T. R. *J. Organomet. Chem.* **1980**, *192*, 139.

(6) For examples, see: (a) Dewar, M. J. S.; Worley, S. D. *J. Chem. Phys.* **1969**, *50*, 654. (b) Dewar, M. J. S.; Worley, S. D. *Ibid.* **1969**, *51*, 263. (c) Worley, S. D. *J. Chem. Soc., Chem. Commun.* **1970**, *980*. (d) Connor, J. A.; Derrick, L. M. R.; Hall, M. B.; Hillier, I. H.; Guest, M. F.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1974**, *28*, 1193. (e) Hall, M. B.; Hillier, I. H.; Connor, J. A.; Guest, M. F.; Lloyd, D. R. *Ibid.* **1975**, *30*, 893. (f) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6443. (g) Lichtenberger, D. L.; Fenske, R. F. *Ibid.* **1976**, *98*, 50. (h) Green, J. C.; Powell, P.; Van Tilborg, J. *J. Chem. Soc., Dalton Trans.* **1976**, 1974. (i) Baerends, E. J.; Oudshoorn, Ch.; Oskam, A. *J. Electron Spectrosc. Relat. Phenom.* **1975**, *6*, 259. (j) Van Dam, H.; Oskam, A. *Ibid.* **1978**, *13*, 273. (k) Van Dam, H.; Oskam, A. *Ibid.* **1979**, *16*, 307. (l) Van Dam, H.; Oskam, A. *Ibid.* **1979**, *17*, 357. (m) Koepke, J. W.; Jolly, W. L.; Bancroft, G. M.; Malmquist, P. A.; Siegbahn, K. *Inorg. Chem.* **1977**, *16*, 2659. (n) Flamini, A.; Semprini, E.; Stefani, F.; Cardaci, G.; Bellachioma, G.; Andreocci, M. *J. Chem. Soc., Dalton Trans.* **1978**, *695*. (o) Egdell, R. G.; Fragala, L.; Orchard, A. F. *J. Electron Spectrosc. Relat. Phenom.* **1978**, *14*, 467. (p) Bursten, B. E.; Fenske, R. F. *Inorg. Chem.* **1979**, *18*, 1760. (q) Cauletti, C.; Clark, J. P.; Green, J. C.; Jackson, S. E.; Fragala, I.; Ciliberto, E.; Coleman, A. W. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 61.

(7) Heilbronner, E.; Jones, T. B.; Krebs, A.; Maier, G.; Malsch, K. D.; Pocklington, J.; Schmelzer, A. *J. Am. Chem. Soc.* **1980**, *102*, 564.

(8) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3290.

(9) Yarkony, D. R.; Schaefer, H. F. *Chem. Phys. Lett.* **1975**, *35*, 291.

(10) For example, see: Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213.

0020-1669/81/1320-1327$01.25/0 © 1981 American Chemical Society

The spectra for (η^5-cyclopentadienyl)(η^3-allyl)molybdenum and tungsten dicarbonyls (C and D, respectively) are quite similar. For both C and D the band assignments are as follows: I_1 at 7.14 or 7.08 eV and I_2 at 7.67 or 7.65 eV, metal d orbital ionization components; I_3 at 8.71 or 8.80 eV, allyl π HOMO; I_4 at 9.52 or 9.66 eV and I_5 at 9.75 or 9.97 eV, cyclopentadienyl π orbitals; I_6 at 10.71 or 10.75 eV, second allyl π orbital. Lichtenberger and Fenske[6g] have reported the UPS of (η^5-cyclopentadienyl)manganese tricarbonyl, and Lichtenberger has recently obtained the UPS of (η^5-methylcyclopentadienyl)manganese tricarbonyl, ethylenedicarbonyl, and propylenedicarbonyl.[11] In contrast to the intriguing observations that the π orbitals of the ethylene and propylene ligands are *destabilized* by complexation with manganese, the π orbitals of the cyclopentadienyl ligand are stabilized (relative to cyclopentadiene at an I_1 of 8.57 eV).[12] The degeneracy of the π HOMO of the ligand is broken by complexation, giving rise to ionization band components at ca. 9.6 and 9.9 eV in the spectrum of (η^5-methylcyclopentadienyl)manganese tricarbonyl. The I_4 and I_5 band components for complexes C and D are very similar in energy and shape to those observed by Lichtenberger which leaves very little doubt in our band assignments. The I_6 component for C and D is rather broad relative to the analogous π allyl component for A and B. This could indicate that the lower π cyclopentadienyl orbital ionization component also lies in this region of the spectrum (the second π ionization energy for cyclopentadiene is 10.62 eV).[12] However, Lichtenberger has observed that the most stable π component for the cyclopentadienyl ligand for manganese complexes occurs at an ionization energy above 12 eV.[11] One notes that the perturbations introduced by the transition metal to the allyl π orbitals are smaller for C and D than they were for A and B. It is possible that this is caused by the presence of the η^5-cyclopentadienyl ligand for C and D rather than by alteration of the transition metal (see earlier discussion).

Finally, it is of interest to compare the current results for η^3-allyl complexes with those obtained by Green et al. for (η^3-allyl)bis(η^5-cyclopentadienyl)niobium[13] and more recently by Fehlner et al. for (η^5-cyclopentadienyl)(η^1-allyl)iron dicarbonyl.[14] For the former complex UPS bands at 8.0 and 8.6 eV were assigned to ionization of the perturbed allyl π orbital and metal/cyclopentadienyl orbitals, respectively; the current work suggests that these assignments should be reversed. For the latter η^1-allyl complex, a band at 9.78 eV is assigned to ionization of the isolated π orbital (analogous to free propylene), while a band at 8.54 eV is assigned to ionization of the Fe–C σ orbital. Thus it would appear that the π HOMO for the η^3-allyl complexes is slightly more stable than is the σ HOMO for the η^1-allyl complex and that the same is true for the lower ligand orbital for the two types of complexes. A reasonable conclusion which might be drawn from this observation is that an η^3-allyl complex should be somewhat more stable than its η^1 analogue, a conclusion that is amply substantiated by experimental observations.[15]

Experimental Section

The photoelectron spectra discussed in this work were obtained on a Perkin-Elmer PS 18 spectrometer. A volatile-inlet probe was employed for complexes A and B, but the solid-inlet probe was used for C and D because temperatures near 70 °C were necessary to obtain suitable spectra. The spectra in Figure 1 represent the average of several runs for each sample. Xenon and argon were always employed as internal calibrants. Compounds A–C were prepared by phase-transfer catalysis;[16] compound D was prepared by the method of Faller et al.[17]

Acknowledgment. S.D.W. gratefully acknowledges the Research Corp. for partial support of this work. We also thank Professors Lichtenberger and Fehlner for communication of their data in advance of publication. Support by the Graduate Research Council and the Arts and Sciences Research committee of the University of Louisville (to D.H.G.) is also gratefully acknowledged.

Registry No. A, 33307-28-7; B, 33307-32-3; C, 12128-87-9; D, 31811-41-3.

---

(11) Lichtenberger, D. L., personal communication.

(12) Derrick, P. J.; Åsbrink, L.; Edqvist, O.; Lindholm, E. *Spectrochim. Acta, Part A* **1971**, *27A* 2525.

(13) Green, J. C.; Jackson, S. E.; Higginson, B. *J. Chem. Soc., Dalton Trans.* **1975**, 403.

(14) Fabian, B. D.; Fehlner, T. P.; Hwang, L.-S. J.; Labinger, J. A. *J. Organomet. Chem.* **1980**, *191*, 409.

(15) McClellan, W. R.; Hoehn, H. H.; Cripps, H. N.; Muetterties, E. L.; Howk, B. W. *J. Am. Chem. Soc.* **1961**, *83*, 1601.

(16) Gibson, D. H.; Hsu, W.-L.; Lin, D.-S. *J. Organomet. Chem.* **1979**, *172*, C7.

(17) Faller, J. W.; Chen, C.-C.; Mattina, M. J.; Jakubowski, A. *J. Organomet. Chem.* **1973**, *52*, 361.

Contribution from the Chemistry Department, University of
South Dakota, Vermillion, South Dakota 57069

Trimethylphosphine–((Dimethylamino)methyl)borane

Maurice J. Byrne and Norman E. Miller*

Received June 25, 1980

The anomalous greater basicity of trimethylphosphine than trimethylamine relative to borane[1] was used to advantage in the preparation of a new borane-derived base, trimethylphosphine–((dimethylamino)methyl)borane (**2**) (eq 1). The

$$Me_3P + \underset{\mathbf{1}}{Me_3N{\cdot}BH_2CH_2NMe_2} \rightarrow Me_3N + \underset{\mathbf{2}}{Me_3P{\cdot}BH_2CH_2NMe_2} \quad (1)$$

known amine analogue, **1**, is prepared from the reaction of *tert*-butyllithium and bis(trimethylamine)dihydroboron(1+) chloride.[2] After 12 h in hexane solution, the reaction with 1:1 to 1.5:1 stoichiometry yields nearly 50% of product which is separated as a clear, colorless liquid, mp −31 to −33 °C, by fractional condensation in a −35 °C trap.

Like **1**, **2** is simultaneously a strong Lewis base and an adduct of another strong Lewis base, this time trimethylphosphine. This feature is the cause of inherent thermal instability toward loss of the $BH_2CH_2NMe_2$ fragment (and its concomitant dimerization) on standing at room temperature. Any process such as bonding to an acid or dissolution in a protonic solvent (water, ethanol) that effectively removes the basic site markedly improves the thermal stability. Under comparable conditions, however, **2** is observably much more stable than **1**. Even toward acid hydrolysis, **2** is also more stable.

An interesting compound of **2** is the borane adduct prepared by contact with diborane in hexane at −78 °C (eq 2). The

$$\mathbf{2} + {}^1/{}_2B_2H_6 \rightarrow \underset{\mathbf{3}}{Me_3P{\cdot}BH_2CH_2NMe_2{\cdot}BH_3} \quad (2)$$

adduct forms as an insoluble solid and is purified by sublimation without decomposition, at 60 °C under high vacuum. This adduct, like the analogous adduct of **1**, has two different dative bonds in the same molecule and does not rearrange to the supposedly stabler adducts $Me_3P{\cdot}BH_3$ and $[(BH_2CH_2NMe)_2]_2$.

---

(1) Stone, F. G. A. *Adv. Inorg. Radiochem.* **1960**, *2*, 279.

(2) Miller, N. E. *J. Organomet. Chem.* **1977**, *137*, 131.