Journal of Organometallic Chemistry, 192 (1980) 139—145

THE ELECTRONIC STRUCTURE OF TRANSITION-METAL CARBONYL COMPLEXES OF NORBORNADIENE AND MESITYLENE

S. D. Worley* and T. R. Webb
Department of Chemistry, Auburn University, Auburn, Alabama 36830 (U.S.A.)
(Received January 11th, 1980)

Summary

The photoelectron spectra of several transition-metal carbonyl complexes of norbornadiene and mesitylene have been measured. The data for the norbornadiene complexes have been compared with those reported previously for norbornadieneiron tricarbonyl. The shifts in energies of the π orbitals of the ligands introduced by the metal carbonyl moieties are remarkably insensitive to the choice of transition metal or geometry of the complex. However, the characters of the metal d-orbital ionization bands are markedly affected by the choice of ligand.

Introduction

There has been a substantial amount of interest recently in the electronic structure of transition-metal carbonyl π complexes of hydrocarbons.[1] Work in these laboratories has centered about the determination of energy shifts for the π orbitals of iron carbonyl complexes of 4π - electron hydrocarbons caused by the perturbing iron carbonyl moiety.[2] In fact it has been demonstrated that the changes in energies for the two occupied π orbitals of such complexes are relatively constant in magnitude over a broad range of ligands.[2] This observation has been used in predicting the π ionization energies of the transient species cyclobutadiene and trimethylenemethane from the photoelectron spectra of their iron tricarbonyl complexes.[2] Recent PES data on the stable molecule tetra-tert-butylcyclobutadiene supports nicely the earlier prediction for cyclobutadiene from these laboratories.[3] Our predicted first ionization energy for cyclobutadiene, which was extrapolated from the PES of the iron carbonyl complex, was 8.29 eV. Heilbronner and coworkers[3] have estimated a value of 8.3 eV for I_1 of cyclobutadiene from the PES of tetra-tert-butylcyclobutadiene; this estimate was obtained by empirical extrapolation of the observed effect of four tert-butyl substituents on a π ionization energy.

The current work represents an extension of these studies to π complexes of molybdenum and chromium. Data on the electronic structures of molybdenum and chromium carbonyl complexes of two ligands, norbornadiene and mesitylene, will be presented. Our reasoning in pursuing this study was to determine the effect of an alteration of transition metal upon the magnitude of the π-orbital energy shifts caused by the perturbing transition-metal-carbonyl moiety.

Results and Discussion

The low-ionization energy regions of the photoelectron spectra of norbornadiene and its iron, molybdenum, and chromium carbonyl complexes are shown in Figure 1. The spectrum of the free ligand norbornadiene contains two well-resolved bands at 8.73 and 9.59 eV which correspond to ionization processes involving the two π orbitals.[2,4] Upon complexation with a metal-carbonyl moiety the highest occupied π orbital for 4π-electron hydrocarbons has been shown to be stabilized by ca. 0.9 eV, while the second π orbital is stabilized by only ca. 0.2 eV.[2] Thus the two π ionization bands for the iron tricarbonyl complex are not clearly resolved. Although in the earlier investigation[2] the π ionization band for this complex was reported as two components (9.63 and 9.80 eV), resolution of the components was poor, and the band peak maximum occurred at ca. 9.73 eV. Resolution of the two components for the molybdenum and chromium complexes is even worse. The band-peak maximum for both of these latter complexes occurs at 9.81 eV. Thus even though the molybdenum and chromium complexes contain four carbonyl ligands while the iron complex only contains three, and Mo/Cr are d^6 transition metals while Fe is d^8, the perturbation of the π orbitals caused by the transition-metal carbonyl moieties is remarkably similar. Furthermore, the first two bands in the photoelectron spectra of all

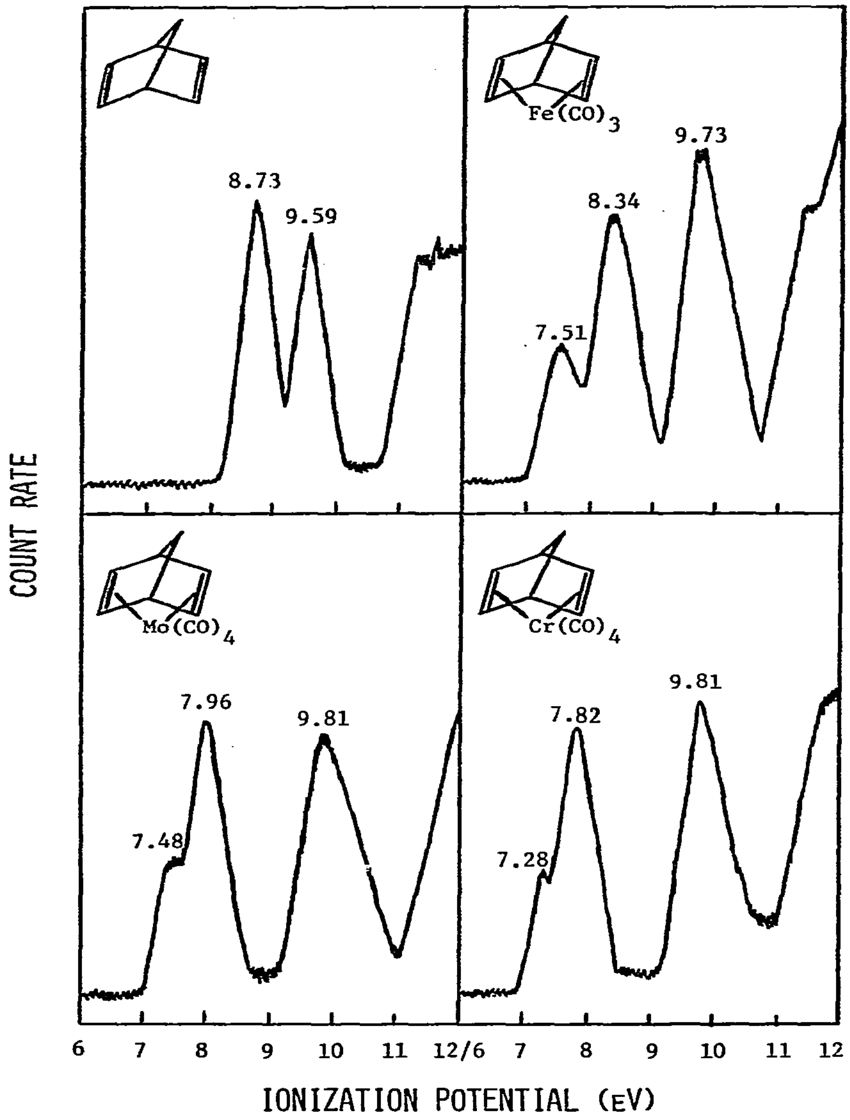

Fig. 1. The photoelectron spectra of norbornadiene and three of its metal carbonyl complexes. The excitation source was the He (I) resonance line.

of the complexes, which refer to ionization processes involving primarily the d-orbital electrons on the transition metals, are similar in character and shape. The splitting between the d-orbital componenets for the iron complex (0.83 eV) is greater than that for the molybdenum (0.48 eV) and the chromium (0.54 eV) complexes, presumably because of the different symmetries of the complexes.

The low ionization-energy regions of the photoelectron spectra of mesitylene and its molybdenum and chromium carbonyl complexes are shown in Figure 2. The first ionization band in the spectrum of mesitylene at 8.45 eV corresponds to an ionization process involving the highest-occupied doubly degenerate π orbital, as previously noted by Koenig and Tuttle.[5] The third π orbital and the highest σ orbital ionization processes are contained under the broad band which has its peak at 11.06 eV. Since the order of these higher ionization processes cannot be assigned definitively, we shall confine our discussion to the band at 8.45 eV. For the two complexes the band at <u>ca</u>. 10.1 eV must correspond to ionization of the perturbed highest-occupied π orbital. Thus the perturbation energy shift for the HOMO is <u>ca</u>. 1.6 eV for both of the transition metal complexes. This perturbation energy is quite a bit higher than was the case for the HOMO of norbornadiene (<u>ca</u>. 1 eV). Of course, this is a consequence of altering the number of π electrons for and symmetry of the ligand. It is noteworthy that there is so little variation in perturbation energy (0.04 eV) between the two different transition metal complexes as was the case for the

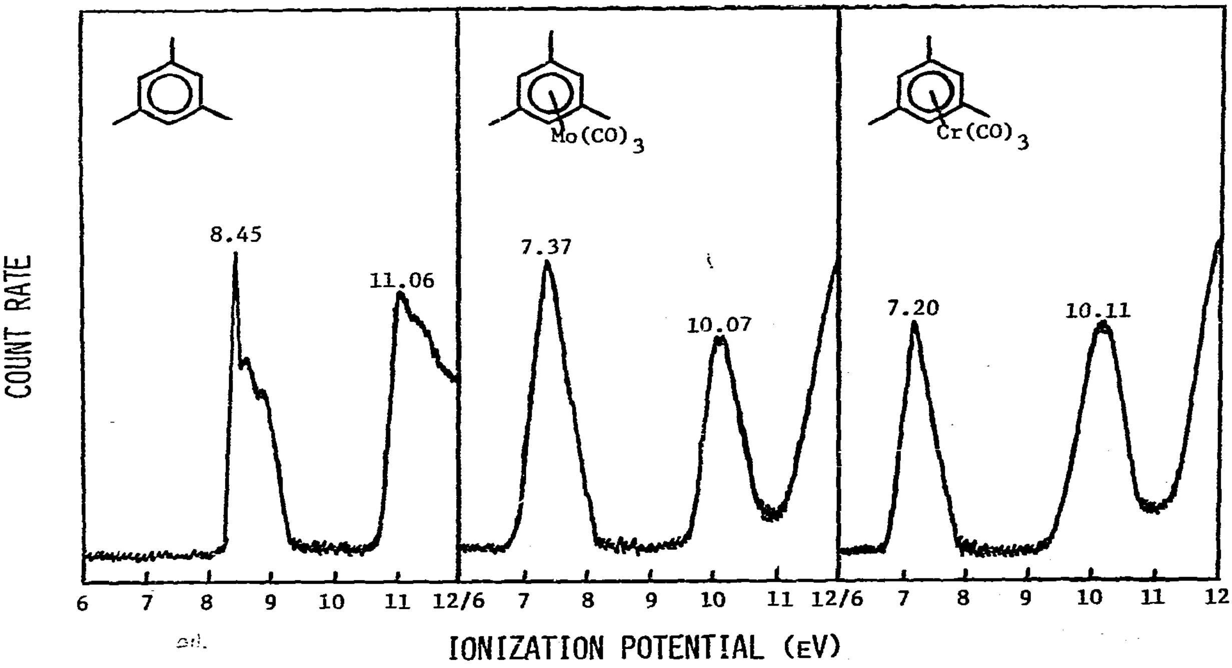

Fig. 2. The photoelectron spectra of mesitylene and two of its metal carbonyl complexes. The excitation source was the He (I) resonance line.

norbornadiene complexes. However, a major difference is noted for the mesitylene complexes in that now all of the d-orbital ionization components are encompased in one unresolved band of the photoelectron spectrum rather than in two resolved components as have been observed for all of the 4π-electron complexes studied previously in these laboratories.[2] One might expect two resolved ionization events for the mesitylene complexes and three for the norbornadiene analogs based upon the expected splitting of the t_{2g}^6 configuration (O_h) under reduced symmetry (C_{3V} and C_{2V}, respectively). Evidently the expected splitting is too small to be resolved for the mesitylene complexes and partially resolved for the norbornadiene analogs. It should be noted that $Cr(CO)_6$ and $Mo(CO)_6$ give photoelectron spectra with a single broad band for the t_{2g}^6 configuration as expected for these molecules having O_h symmetry; however, chromocene does give rise to a spectrum with several d-orbital ionization components.[6]

Conclusion

Our data from the PES of several gas-phase transition-metal carbonyl complexes of norbornadiene and mesitylene have shown that the electronic structures of the ligand moieties are remarkably insensitive to the choice of transition metal. This is not the case, however, for the metal d-orbital electronic structure. The splittings and energies of the ionization components corresponding to the metal d-orbital electrons do change appreciably when the ligand is altered. It should be noted that Mann has also observed little difference in the electronic environments of the ligands norbornadiene and mesitylene for the chromium and molybdenum carbonyl complexes in the solution phase (^{13}C nmr data).[7]

Experimental

The complexes used in this work were prepared by refluxing the appropriate hexacarbonyl with norbornadiene or mesitylene.[8] Purification was accomplished by recrystallization and sublimation; the purified products were characterized by infrared spectroscopy and ^1H nmr.

The photoelectron spectra discussed here were measured by a Perkin-Elmer PS-18 spectrometer equipped with a heated-inlet probe. In all cases He I excitation was used, and argon and xenon were employed as internal calibrants. The data represent an average of several spectra for each sample. The transition-metal-carbonyl complexes are involatile solids at room temperature, but suitable spectra were obtained by heating the ionization chamber of the spectrometer to ca. 50° for the norbornadiene complexes and to 60-80° for the mesitylene complexes. The samples did not change color or character upon this heating process, so we feel that sample decomposition was minimal.

Acknowledgements

S. D. Worley gratefully acknowledges support provided by the Research Corporation for this work. T. R. Webb gratefully acknowledges the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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