Journal of Organometallic Chemistry, 191 (1980) 409—413
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ALLYLIC INTERACTIONS IN ORGANOMETALLICS: PROBING ELECTRONIC STRUCTURE IN $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$, R = CH_3, $\eta^1\text{-}C_3H_5$, $\eta^1\text{-}C_5H_5$.

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(Received November 15th, 1979)

Summary

The He(I) photoelectron spectra of $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$, where R = CH_3, $\eta^1\text{-}C_3H_5$ and $\eta^1\text{-}C_5H_5$, have been recorded. The lowest lying ion states result from ionization of molecular orbitals with large Fe *3d* character; these move to lower energy when R places double bonds in an allylic relationship to the metal atom. The cyclic voltammetric oxidation potential correlates well with the energies of the lowest ion states. A significant interaction between olefin π orbitals and the allylic metal center is proposed.

Introduction

The presence of an allylic double bond in a transition metal alkyl has been noted to result in qualitative changes in chemical behavior. For example, whereas protonation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$, ($FpCH_3$, I) leads to Fe—C bond cleavage, the related compounds Fp(η^1-allyl) (II) and Fp(η^1-cyclopentadienyl) (III) protonate at the double bond to give olefin complexes [1]. Similarly, anomalous phosphine substitution reactions of III [2] have been interpreted in terms of radical addition to the double bonds [3]. In this work we have examined complexes I—III by means of ultraviolet photoelectron spectroscopy and cyclic voltammetry in order to investigate quantitative effects resulting from the interaction (if any) between metal centers and allylic unsaturated groups.

Experimental

The photoelectron spectrometer used has been previously described [4]. Samples of I—III, purified by vacuum sublimation, distillation or column chromatography, respectively, were introduced into the spectrometer at room temperature.

Initial spectra of III showed signals due to ferrocene (which is more volatile than III); however, these peaks disappeared after the first few runs. The ^1H NMR spectrum of sample remaining after data collection showed that ferrocene contamination was no longer present. The spectrometer was operated at a resolution of 20 meV (FWHM) at 5 eV electron energy and a number of spectra were run for each compound using a Xe-Ar mixture for internal calibration.

Cyclic voltammetric experiments were carried out with a cell designed for inert-atmosphere operation [5], using a PAR model 173 potentiostat in conjunction with a PAR model 175 programmer and a Houston Instrument model 200 x-y recorder. Solutions contained ca. 1—2 m*M* compound and 0.05 *M* Bu_4NBF_4 in THF (freshly distilled from sodium benzophenone ketyl under argon). A Pt wire working electrode and saturated calomel reference electrode were used, with scan rates from 50—500 mV/sec. Under these conditions the separation between peaks in the cyclic voltammogram of ferrocene, a known reversible couple, was considerably greater than the theoretical value, probably because of slow recorder response. Since this would lead to substantial change in the peak position of the (irreversible) waves here, $E_{1/2}$ values were used instead.

The Slater exponents and ionization potentials used in the EHMO calculations (6) follow: Fe, 3*d* 2.600, —11.67; 4*s* 0.970, —9.75; 4*p* 1.625, —5.89. C, 2*s* 1.625, —21.40; 2*p* 1.625, —11.40. O, 2*s* 2.275, —32.30; 2*p* 2.275, —14.80. H 1*s* 1.300, —13.60. Accepted average bond distances were used in these calculations.

Results and discussion

The bands of lowest ionization potential (i.p.) in the He(I) photoelectron spectra of I—III are shown in the Figure and the data are summarized in Table 1. The spectrum of I has been reported by three independent groups [7—9] and i.p.'s in the various determinations agree satisfactorily. There has been some disagreement about assignments: while the band at lowest i.p. is assigned as arising from two metal *d* orbitals, the next two bands are assigned as arising from Fe—C bonding and metal *d* respectively [7] or vice-versa [8,9]. The latter appears more justifiable on the grounds of both peak shape and intensity [9] as well as by comparison to related compounds [8,9] and is taken to be correct in this work.

The empirical assignment of II and III begins with the observation that the π i.p.'s of propene and cyclopentadiene are 9.73 eV ($2a''$), and 8.58 eV ($1a_2$) and 10.62 eV ($2b_1$) respectively [10]. These i.p.'s should not change greatly in going to II and III; thus the band with fine structure (ca. 1100 cm^{-1}) at 9.78 eV in II and the bands at 8.76 and 11.00 eV in III are assigned to the olefinic π i.p.'s expected. The orbitals associated with the Fe—η^5-C_5H_5 interaction should be relatively insensitive to changes in the alkyl group; hence, the bands at 10.24 eV in II and at 10.20 eV in III are so assigned. By difference, bands 1 and 2 in each spectrum must contain the three metal *d* i.p.'s and the Fe—C i.p.. Consideration of relative band areas in I—III suggests the assignment for bands 1 and 2 given in Table 1 which, although reasonable, is not unambiguous. This ambiguity does not, however, affect the conclusion that the i.p.'s of the bands

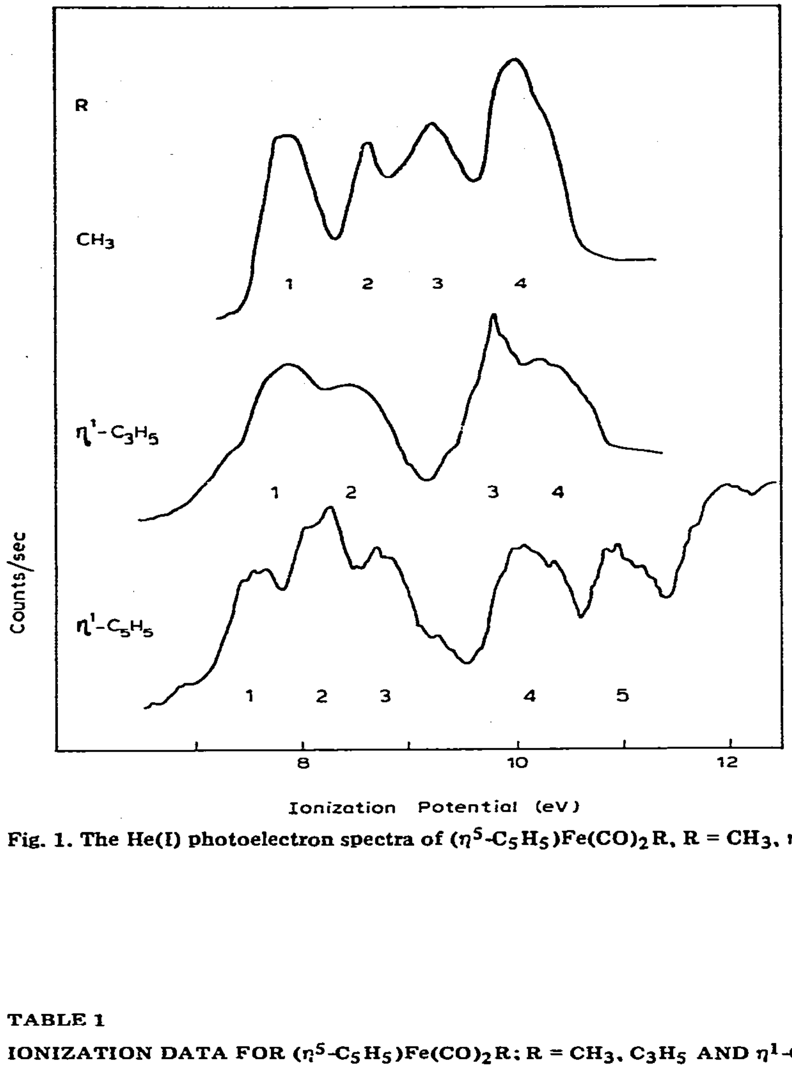

Fig. 1. The He(I) photoelectron spectra of (η^5-C_5H_5)Fe(CO)$_2$R, R = CH_3, η^1-C_3H_5, η^1-C_5H_5.

TABLE 1

IONIZATION DATA FOR (η^5-C_5H_5)Fe(CO)$_2$R; R = CH_3, C_3H_5 AND η^1-C_5H_5

R	Band [a]	Vertical [b] I.P. (eV)	*A/E* [c]	Assignment (No. ip's)
CH_3	1	7.91	0.56	Fe 3*d* (2)
	2	8.56	0.37	Fe 3*d* (1)
	3	9.21	0.59	Fe—C σ (1)
	4	9.94	1.00	Fe—πC*p* (3)
C_3H_5	1	7.97	1.00	Fe 3*d* (3)
	2	8.54	0.77	Fe—C σ (1)
	3	9.78	0.90	π C_3H_5 (1)
	4	10.24	1.00	Fe—π Cp (3)
η^1-C_5H_5	1	7.58	0.56	Fe 3*d* (2)
	2	8.18	0.96	Fe 3*d* (1) + Fe—C σ (1)
	3	8.76	0.75	π C_5H_5 (1)
	4	10.20	1.00	Fe—π Cp (3)
	5	11.00	0.93	π C_5H_5 (1)

[a] See Fig. 1 for numbering. [b] Energies refer to band centers. [c] Relative area divided by electron energy.

TABLE 2

COMPARISON OF IONIZATION AND OXIDATION POTENTIALS (eV)

	I	II	III	Δ, I → II	Δ, II → III
$E_{1/2}$ [a]	1.15	0.90	0.75	−0.25	−0.15
Fe(*d*) + Fe—C, av	8.40	8.11	7.88	−0.29	−0.23
Fe(*d*)av	8.18	7.97	7.78	−0.21	−0.19
Fe—C	9.21	8.57	8.18	−0.67	−0.36

[a] Measured as described in Experimental section; all three compounds gave completely irreversible oxidation peaks at all scan rates examined.

resulting from ionization of the orbitals with highest metal character decrease along the series I → II → III.

If we look at the weighted average of all four lowest i.p.'s, the weighted average of the 3 Fe *d* i.p.'s or the Fe—C i.p (Table 2), we find a smooth decrease on going from I → II → III. This decrease is exactly mirrored in the oxidation potentials for these three compounds, which decrease in the same order and by roughly the same amount. This agreement is quite reasonable as electrochemical and chemical oxidations of compounds such as I appear to involve oxidation at the metal [11]. Experimentally it is clear that the presence of allylic double bonds reduces the energy required to oxidize the metal center. This may be contrasted with the effect of a cyano group in $FpCH_2CN$, in which the Fe *d* and Fe—C i.p.'s are significantly greater than in I [8], reflecting the electron withdrawing ability of —CN.

It is worthwhile to explore the reasons behind the observed trend in energetics. The decrease in the Fe—C i.p. from I to III can be empirically understood in terms of simple substitution on the α carbon. For example, ionization from Hg—C bonding orbitals shows a decrease of 0.5 eV from MeHg—Me to MeHg—Et, and 0.4 eV from the latter to MeHg—i-Pr [12], not unlike the changes observed here. The similar decrease in the i.p.'s of the other metal *d* orbitals cannot be explained in terms of increased substitution on R since saturated substituted derivatives FpR ($R = CH_2SiMe_3$, CH_2Ph, CH_2CH_2Ph) show higher oxidation potentials than FpMe [11]. Therefore, the lowering of the oxidation potential for II and III, and the corresponding decreased i.p. for the Fe *d* orbitals, must be a specific consequence of the olefinic double bonds in the R groups.

The exact nature of the metal—allylic double bond interaction can only be explored further on the basis of a theoretical model. Thus, we have carried out extended Hückel-type calculations for the three compounds. Although the results of this relatively simple calculational method do not completely reproduce the orbital ordering established by the photoelectron spectra, they do correctly predict the orbitals discussed above to be the highest lying orbitals *. Of key interest is that the orbitals in II and III which are primarily olefin in character are found to have substantial amounts of metal *d* character mixed in. For example, in II this MO contains 45% $C_{2p\pi}$ and 10% Fe_{3d}. Thus in contrast to saturated derivatives, this mixing provides a mechanism for the positive charge

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* The MO's with large metal character are found to be ca. 2 eV too stable with respect to the ligand orbitals.

on the metal in the cation to be partially delocalized to the double bond, thereby stabilizing the final state in the ionization process. In this regard the situation is similar to the ionization of an allylic halide with respect to a saturated halide. It must be kept in mind, however, that the type of calculation employed tends to emphasize mixing of orbitals, especially in low-symmetry cases such as these considered here; it would be of interest to see whether more powerful techniques give this result as well.

The chemical importance of this interaction (aside from the small decrease in oxidation potential observed) is not yet clear, but one might consider the facile fluxional processes (η^1—η^3 allyl interconversion; ring whizzing of η^1-C_5H_5) frequently observed in compounds of this type. The question of whether transition metal organometallics should obey orbital symmetry rules worked out for organic compounds, or whether the involvement of *d* orbitals provides a mechanism for relaxing these rules, has been of considerable interest [13,14]. While the 1,2-shift in III is indistinguishable from the allowed 1,5 sigmatropic migration [14], it has very recently been found that (η^1-C_7H_7)Re(CO)$_5$ also rearranges via 1,2 shifts [15], in contrast to the allowed 1,5 path established for the main-group analog (η^1-C_7H_7)SnPh$_3$ [16]. In this case, then, the transition metal system does not obey the orbital symmetry rules. Since our findings are that in such compounds the metal *d* orbitals do in fact mix with the π-system of the organic moiety, this apparent violation may be quite reasonable.

Acknowledgements

The support of the National Science Foundation through Grant CHE79-15220 (T.P.F.) and the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society (J.A.L.), are gratefully acknowledged. The electrochemical equipment was purchased with funds from the Research Corporation (J.A.L.). We also wish to thank Professor Roger DeKock, Calvin College, Grand Rapids, MI, for advice in performing the Hückel calculations.

References

1 A. Davison, N. McFarlane, L. Pratt and G. Wilkinson, J. Chem. Soc., (1962) 3653; M.L.H. Green and P.L.I. Nagy, J. Chem. Soc., (1963) 189; M.L.H. Green and P.L.I. Nagy, Z. Naturforsch, 18b (1962) 162.
2 J.A. Labinger, J. Organometal. Chem., 136 (1977) C31.
3 B.D. Fabian and J.A. Labinger, J. Amer. Chem. Soc., 101 (1979) 2239.
4 T.P. Fehlner, Inorg. Chem., 14 (1975) 934.
5 J.B. Headridge, Electrochemical Techniques for Inorganic Chemists, Academic Press, New York, 1969, p. 16.
6 R. Hoffmann, J. Chem. Phys., 39 (1963) 1397; R. Hoffmann and W.N. Lipscomb, ibid., 36 (1962) 3489.
7 D.A. Symon and T.C. Waddington, J. Chem. Soc., Dalton Trans., (1975) 2140.
8 J.C. Green and S.E. Jackson, J. Chem. Soc., Dalton Trans., (1976) 1698.
9 P.C. Lichtenberger and R.F. Fenske, J. Amer. Chem. Soc., 98 (1976) 50.
10 G. Bieri, F. Burger, E. Heilbronner and J.P. Maier, Helv. Chem. Acta, 60 (1977) 2213.
11 W. Rogers, J.A. Page and M.C. Baird, J. Organometal. Chem., 156 (1978) C37.
12 T.P. Fehlner, J. Ulman, W.A. Nugent and J.K. Kochi, Inorg. Chem., 15 (1976) 2544.
13 See, for example, C-C Su, J. Amer. Chem. Soc., 93 (1971) 5653 and references therein.
14 F.A. Cotton, in L.M. Jackman and F.A. Cotton (Eds.), Dynamic Nuclear Magnetic Resource Spectroscopy, Academic Press, New York, 1975, pp. 700—701.
15 P.M. Heinekey and W.A.G. Graham, J. Amer. Chem. Soc., 101 (1979) 6115.
16 R.B. Larrabee, J. Amer. Chem. Soc., 93 (1971) 1510; B.E. Mann, B.F. Taylor, N.A. Taylor and R. Wood, J. Organometal. Chem., 162 (1978) 137.