stability of (*S*)-(+)-1-NpPhMeSiF under the same experimental conditions has been tested. By the above procedure, 0.11 g (1 mmol) of difluorogermylene was allowed to react in 10 mL of dioxane with 0.28 g (1 mmol) of (*S*)-(+)-1-NpPhMeSiF,[17] $[\alpha]_D$ +47°. Pentane extraction of residue yielded 0.25 g of 1-NpPhMeSiF, $[\alpha]_D$ +15.1° (in pentane, 68% racemization).

Registry No. **2a**, 86885-11-2; **2b**, 86885-12-3; **2c**, 86885-13-4; **2d**, 86885-14-5; **2e**, 21863-04-7; **3**, 12086-96-3; **5**, 86885-15-6; **6**, 14095-19-3; **10** (Y = I), 86885-18-9; **10a**, 86885-16-7; **10b**, 86885-17-8; **11**, 5764-63-6; **12**, 86885-19-0; **13**, 86885-20-3; **15**, 86885-21-4; **16**, 63976-34-1; **17**, 75247-27-7; $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$, 38117-54-3; $Co_2(CO)_8$, 15226-74-1; $[Ph_3P(CO)_3Co]_2$, 24212-54-2; $[(PhO)_3P\text{-}(CO)_3Co]_2$, 21118-36-5; $Mn_2(CO)_{10}$, 10170-69-1; $(\eta\text{-}C_5H_5)\text{-}(CO)_2Fe\text{–}Mo(CO)_3(\eta\text{-}C_5H_5)$, 12130-13-1; $(\eta\text{-}C_5H_5)(CO)_2Fe\text{–}Mn\text{-}(CO)_5$, 12088-73-2; $NaCo(CO)_4$, 14878-28-5; GeF_2, 13940-63-1; PhGeCl, 32329-21-8; PhBr, 108-86-1; Ph_3SiF, 379-50-0; (*S*)-(+)-1-NpPhMeSiF, 13132-41-7; 2,3-dimethylbutadiene, 513-81-5.

He I and He II Photoelectron Spectra of Substituted (Cycloheptatriene)tricarbonyliron Complexes $(\eta^4\text{-}exo\text{-}7\text{-}RC_7H_7)Fe(CO)_3$ (R = H, $SiMe_3$, $GeMe_3$)

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He I and He II photoelectron spectra of $(\eta^4\text{-}RC_7H_7)Fe(CO)_3$ (R = H, $SiMe_3$, $GeMe_3$) have been studied in order to identify possible electronic factors responsible for the variation in fluxional behavior in the series. Spectral evidence indicates that there is a rupture in conjugation between the free double bond and the bound butadiene moiety and a stronger Fe–diene interaction in the substituted compounds relative to the unsubstituted molecules. These effects appear to be sufficient to cause a significant lowering of the activation energy for 1,3 iron shifts in the silyl- and germyl-substituted compounds.

Introduction

The reaction of $[(\eta^3\text{-}C_7H_7)Fe(CO)_3]^-$, an interesting and rare example of ambident organometallic nucleophile, with Me_3SiCl and Me_3GeBr yields ring-substituted complexes $[\eta^4\text{-}exo\text{-}7\text{-}(Me_3E)C_7H_7]Fe(CO)_3$ (E = Si, **2**; E = Ge, **3**).[1] The molecules exhibit surprisingly facile fluxional motion of the $Fe(CO)_3$ moiety, the activation energy for the 1,3 iron shift being some 5 kcal/mol lower than in the unsubstituted parent compound $(\eta^4\text{-}C_7H_8)Fe(CO)_3$[1,2] (**1**). An obvious question that arises is how this behavior relates to some relevant modification in the electronic structure of the complexes upon C_7 ring substitution by the EMe_3 moieties?

To answer this question we have embarked on an investigation of both parent and ring-substituted complexes using gas-phase UV photoelectron spectroscopy (PE). The He I spectrum of $(\eta^4\text{-}C_7H_8)Fe(CO)_3$ complex has been reported already.[3] This paper, however, includes both He I and He II spectra. The comparison of He I vs. He II relative intensity variations of bands present in the low ionization energy (IE) region has proven of crucial relevance for a critical analysis of the previous interpretation[3] and, thereore, has provided a more adequate rationale for the interpretation of PE data of present substituted complexes.

Results and Discussion

Figure 1 shows the PE spectrum of **1**. Three main features (labeled a,b, and c) can be identified in the region up to 11.5 eV. The He I spectrum is in good agreement with the previous study of Green et al.[3] (see also Table I). Notable differences in the relative spectral intensities are observed when the radiation is changed to He II. The band envelope a increases remarkably relative to all the bands that follow in the spectrum.

The spectra of the ring-substituted complexes **2** and **3** (Figures 2 and 3) are markedly different from those of **1**. The feature around 8 eV now contains only two somewhat resolved bands. The next spectral region up to 11.5 eV consists of an ill-resolved structure where four distinct ionizations are evident in the form of peaks or shoulders (see Table I). In the HeII spectra, in analogy to **1**, the onset band system a increases in relative intensity.

In the higher region (not shown in the figures) the spectra all show poorly resolved structures that are characteristic of systems containing cyclic polyolefin and carbonyl ligands. They represent ionizations from inner π and σ orbitals that are practically not involved in the metal–ligand bonding.

The assignment of present spectra can conveniently start with that of the simpler **1**. On the basis of He I data, Green et al.[3] assigned the first two peaks a and a′ to ionizations of metal 3d electrons. The following three peaks were thought to represent ionizations from ring π molecular orbitals (MO's).

Within the framework of Gelius' model[4] of PE cross sections, the present data, unfortunately, argue for a different interpretation. The identical He II vs. He I relative intensity growth of bands a, a′, and a″ points to an almost

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(1) (a) LiShingMan, L. K. K.; Takats, J. *J. Organomet. Chem.* **1976**, *117*, C104. (b) Deganello, G.; LiShingMan, L. K. K.; Reuvers, J. G. A.; Takats, J. *Organometallics* **1983**, *2*, 28.

(2) Karel, K. J.; Albright, T. A.; Brookhart, M. *Organometallics* **1982**, *1*, 419.

(3) Green, J. C.; Powell, P.; Van Tilborg, J. *J. Chem. Soc., Dalton Trans.* **1974**, 1975.

(4) Gelius, U. "Electron Spectroscopy"; Shirley, D. E., Ed.; North-Holland Publishing Co.: Amsterdam, 1972; p 311.

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Table I. Ionization Energies (eV) and Assignments of the Studied Complexes[a]

$Fe(C_7H_8)(CO)_3$	assignt	$Fe[C_7H_7Si(CH_3)_3](CO)_3$	$Fe[C_7H_7Ge(CH_3)_3](CO)_3$	assignt
(a) 7.74	Fe 3d	(a) 7.96	(a) 7.62	Fe 3d
(a′) 8.42		(a′) 8.56	(a′) 8.35	
(a″) 8.85				
		(b) 10.13	(b) 9.75	σ(E–C) (E = Si, Ge)
(b) 10.29	π_1	(b′) 10.90	(b′) 10.40	π_1
(c) 11.10	π_2	(c) 11.20	(c) 10.92	π_2
(d) 11.86	π_3	(d) 11.87	(d) 11.81	π_3

[a] Band labels reported in the figures are reported in brackets.

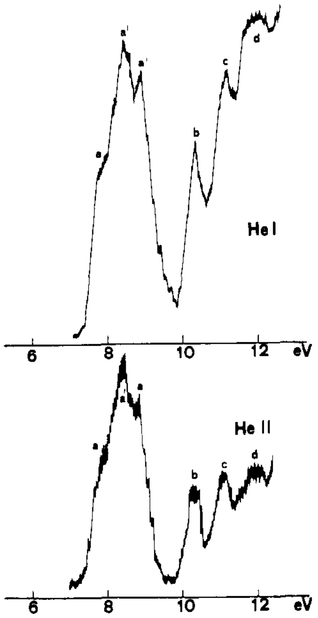

Figure 1. He I and He II photoelectron spectra of (η^4-C$_7$H$_8$)-Fe(CO)$_3$, **1**.

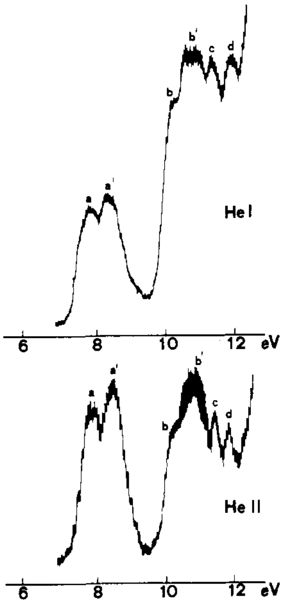

Figure 2. He I and He II photoelectron spectra of [η^4-*exo*-7-(Me$_3$Si)C$_7$H$_7$]Fe(CO)$_3$, **2**.

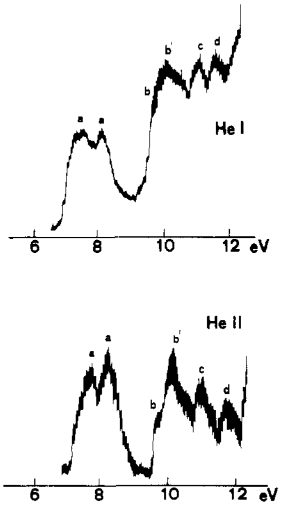

Figure 3. He I and He II photoelectron spectra of [η^4-*exo*-7-(Me$_3$Ge)C$_7$H$_7$]Fe(CO)$_3$, **3**.

identical nature of corresponding MO's and, in particular, to a dominant metal 3d character. In fact, the He II cross section of Fe 3d subshells has been found to be considerably greater than that of carbon 2p orbitals.[5a] In reality any alternative assignment of band a″ in terms of ionization of the ring π MO must be dismissed, since even in the case of significant admixture with Fe 3d orbitals, the He II cross section of C 2p based MO's has been found much smaller than encountered in the present case.[5a]

Given this assignment for the band envelope a, we are left with bands b, c, and d for the ionizations of the three more external π MO's (hereafter π_{1-3}).

It is worth to note that the electronic structure of the simple (cycloheptatriene)iron tricarbonyl and of some C$_7$-substituted derivatives has been recently examined by Albright in a very elegant study.[2] The Hückel analysis of **1** suggested a ground-state MO ordering in which the energies of ligand-based MO's π_1 and π_2 lie between those of metal-based orbitals related to octahedral e$_g$ and t$_{2g}$ sets.[6] This ordering is different than that afforded by present PE data which indicates that the metal 3d ionizations are all grouped in the onset band envelope a. Nevertheless, upon ionization differential relaxation energies among π_1, π_2, and metal orbitals related to the t$_{2g}$ set are expected[5a,b] to be large enough to upset the small energy separation (<1 eV)[2] between the two groups of orbitals, thus giving the sequence of final states observed in the PE experiment. With regard to the presently proposed assignment, several observations can be made. The splitting of 3d subshells in three well-separed components at variance to the doublet pattern observed in the case of other (cycloheptatriene)tricarbonylmetal complexes having η^6- ring ligation[7] can be related to the η^4 ligation in the present iron complex and, hence, to the lower local symmetry. Furthermore, the peculiarity of the ring ligation mode can account safely for the different trend of IE's of π_{1-3} MO's than observed in more symmetric complexes. The com-

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[5] (a) 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. (b) Guest, M. F.; Hillier, I. H.; Higginson, D. R.; Lloyd, D. R. *Mol. Phys.* **1975**, *29*, 113.

[6] In the Albright paper[2] these MO's are referred as 2e$_a$ (Fe 3d, e$_g$), 2π_s and 1π_a (π_1 and π_2), and le$_s$, le$_a$, and 1a$_1$ (Fe 3d, t$_{2g}$).

[7] Fragalà, I.; Ciliberto, E.; Granozzi, G.; Deganello, G. *J. Organomet. Chem.* **1979**, *182*, 511.

parison of present IE data with those of, for instance, $(\eta^6\text{-}C_7H_8)Cr(CO)_3$ reveals that the IE associated with the π_1 MO moves considerably toward higher IE values whereas those associated with the π_{2-3} MO's stay almost constant.[7] A related consequence is the reduced energy separation $\Delta E(\pi_1\text{–}\pi_3)$. This trend agrees well with that due to a major rupture of the conjugation within the ring trienic framework because of the η^4 ligation.[8]

It seems reasonable to assume that a similar MO sequence governs the spectra of the ring-substituted derivatives as well. There is no doubt that the first two bands a and a′ in Figures 2 and 3 represent ionizations of metal 3d electrons. The remarkable increase of the relative intensity of these bands under the He II radiation is entirely in accord with this. However, the profile of this band system is quite different than the corresponding spectral area in the spectrum of 1, only two peaks being now discernible. Consequently, the ionizations from the π_{1-3} MO's must originate from the ill-defined structure between 9.5 and 12 eV. An unambiguous assignment of these latter bands is very difficult, and the task is further complicated by the fact that ionizations from the σ(Si–C) and σ(Ge–C) orbitals are also expected to occur in this energy region. Literature data[9] suggest a value of 10.2 eV for the σ(Si–C) ionization and a slightly lower value for that of the σ(Ge–C) orbital. Thus, we may identify these ionizations with the shoulders at 10.13 and 9.75 eV in spectra of 2 and 3, respectively. Obviously the remaining bands b, c, and d in this region must represent ionizations from the π_{1-3} MO's.

Given this assignment it becomes evident that the ring substitution results in a remarkable perturbation both of metal 3d subshells and of ring π MO's. In particular we note (Table I) a coalescence of metal ionization into a narrower range than in the unsubstituted complex, some stabilization (more relevant in the case of 2) of the π_1 MO, and, finally, practically no changes as far as the ionizations of π_2 and π_3 MO's are concerned. The first of these observation seems particularly interesting since the doublet structure of Fe 3d ionizations is strongly reminiscent of the pattern observed in large series of (diene)iron tricarbonyl complexes, the energy separation between the two components (0.6–0.7 eV) being also very close to values quoted for mentioned diene complexes.[10] It is tempting to correlate this observation with a stronger "iron–diene" bonding in complexes 2 and 3 than in 1 and, consequently, with a more pronounced rupture of the conjugation between the complexed diene system and the remaining double bond. Such interpretation is consistent with the single-crystal X-ray data of the Ph_3Ge-substituted material.[1b,11]

The stabilization of π_1 MO in both 2 and 3 points to a stronger interaction (than in 1) of this MO with empty metal orbitals and, hence, again to a stronger metal–ligand bonding. Identical conclusions are arrived at by the analysis of He I vs. He II intensity pattern of the band related to the ring π_1 orbital in spectra of 2 and 3. It turns out that the band b′ increases in the He II spectra relative to all the other bands of the envelope thus indicating some metal 3d contribution in the corresponding MO. Interestingly this behavior finds no counterpart in the He II spectrum of 1. Therefore, the enhanced metal–ligand interaction must be, in some way, related to the perturbation of the C_7 ring substituents. In accord with the Albright's theoretical model,[2] we assume that the main perturbarion introduced at C_7 is due to the high-lying filled orbital ($\sigma_{E\text{-}C}$) of the $-ER^3$ fragment. This orbital, symmetrical with respect to the ring mirror plane, can affect the π_1 ring orbital only.[2] Furthermore the discussed trend of spectral data on passing from 1 to 2 and 3 becomes understandable within a model by which the perturbation destabilizes (relative to C_7H_8) the π_1 orbital in the free $C_7H_7ER_3$ ligands.[12] Therefore its closer approach to the energy[13] of the unperturbed LUMO of the $-Fe(CO)_3$ fragment finally results in a better interaction and, hence, in the observed stronger metal–ligand interaction. These conclusions are borne out by X-ray structural work and are indeed consistent with the well-established electron-donating ability of silyl or germyl groups especially when they are β to an unsaturated system.[14,15]

Finally, we would like to comment on the variations in electronic structures on passing from 1 to 2 and 3 and their relation to the observed dynamic behavior. First of all, apparently small substitutional changes are sufficient to impart significant modifications in the ring π system. In particular this gives rise to some localization of the free double bond adjacent to the 7 substituent and hence inequivalence, in terms of charge density, among the ring carbon atoms. A strictly related effect is a stronger and more asymmetric bonding of the $-Fe(CO)_3$ unit to the ring diene system in compounds 2 and 3 in accord with the Albright model.[2] Such effects have resulted in the lowering of the energy barrier for 1,3 metal shifts in complexes 2 and 3 relative to the unsubstituted complex 1.

Experimental Section

The compounds $Fe(C_7H_8)(CO)_3$, $Fe[C_7H_7Si(CH_3)_3](CO)_3$, and $Fe[C_7H_7Ge(CH_3)_3](CO)_3$ were prepared and purified according to published procedures.[1b] The PE spectra were measured on a Perkin-Elmer PS/18 spectrometer modified by inclusion of a hollow cathode source giving a high output of He II photons (Helectros Development). The spectra were calibrated by admixture of inert gases (Xe, N_2) and by reference to the He($1s^{-1}$) self-ionization.

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Registry No. 1, 36343-88-1; 2, 83006-17-1; 3, 83058-33-7.

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[8] For a collection of IE data on various polyolefin see, for example: Batich, C.; Bischof, P.; Heilbronner, E. *J. Electron Spectrosc. Rel. Phenom.* **1973**, *1*, 333.

[9] (a) Evans, S.; Green, J. C.; Jackson, S. E. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 191. (b) Evans, S.; Green, J. C.: Joachim, P. J.; Mayer, J. P.; Orchard, A. F.; Turner, D. W. *Ibid.* **1972**, *68*, 905.

[10] (a) Worley, S. D.; Webb, T. R.; Giboon, D. H.; Ong. T. S. *J. Electron Spectros. Rel. Phenom.* **1980**, *18*, 189–98. (b) Worley, S. D.; Webb, T. R. *J. Organomet Chem.* **1980**, *192*, 139.

[11] The structure of 3 has been determined also. However, the precision of C–C distances is such that it is unwise to speculate on this aspect of the structure.

[12] It must be noticed that the present PE data (Table I) indicate that the σ (E–C) orbital lies higher than π_1 in 2 and 3. Nevertheless, the closer energies of the two orbitals suggest that their ordering can be upset in the free ligand, the inversion observed in 2 and 3 being mediated by metal–ligand interactions.

[13] The enhancement of metal–ligand interactions in complexes 2 and 3 must depend upon a better energy matching of interacting orbitals since C_7 substitution cannot influence overlap factors.

[14] Mollère, P.; Bock, H.; Becker, G.; Fritz, G. *J. Organomet. Chem.* **1972**, *46*, 89.

[15] Ramsey, B. "Electronic Transition in Organometalloids"; Academic Press: New York, 1969