

implies two possibilities for the arrangement of the tetrahydrofuran ring, which are statistically distributed over the crystal. Figure 3 contains both possibilities, marked with the different numbering of the tetrahydrofuran carbon atoms (C20, C22, and C23 for one ring and C20', C22', and C23' for the other one). The lutetium oxygen distance (226.5 pm) is in the same range as in 8.

The lutetium-carbon σ -bond lengths are 237.6 pm in 8 and 234.5 pm in 10, about 10 pm shorter than in $[\text{Li}(\text{THF})_4][\text{Lu}(\text{C}_6\text{H}_3\text{Me}_2)_4]$ with 245 pm²⁶ and $(\text{C}_5\text{H}_5)_2\text{LuC}(\text{CH}_3)_3(\text{THF})$ with 247 pm¹⁶ because of the less crowded situation in 8 and 10 compared with that in the other two complexes. The surprisingly large bond angle of 130.7° at C1 in 8 is determined by the spatial requirement of the trimethylsilyl group bound to the same carbon atom and the cyclopentadienyl and tetrahydrofuran ligands around lutetium. A similar large bond angle at an α -carbon atom was noted for the surrounding of the CH₂ carbon in $[(\text{CH}_3)_3\text{CCH}_2]_3\text{Ta}\equiv\text{CC}(\text{CH}_3)_3\text{Li}(\text{dmp})$.³⁰

Reactivity. The new compounds are extremely sensitive toward moisture and oxygen. On hydrolysis all the ligands are replaced from the lanthanides with formation of $\text{Ln}(\text{OH})_3$, cyclopentadiene, and the appropriate hydrocarbon. In the case of 8, 8a, 8b, and 8c, tetramethylsilane can be detected in the NMR spectrum of the decomposition products. All compounds decompose above 120 °C

first with liberation of tetrahydrofuran. The *tert*-butyl-lutetium complex 6 then undergoes further decomposition via a β -elimination process, to yield 2-methylpropane and 2-methylpropene, whereas 8 gives tetramethylsilane. Above 200 °C $\text{Lu}(\text{C}_5\text{H}_5)_3$ is formed via intermediate organolutetium hydride formation.^{17,31}

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Registry No. 1, 82293-69-4; 2, 76207-05-1; 3, 76207-06-2; 4, 82293-70-7; 5, 76207-07-3; 6, 76207-08-4; 6a, 82293-71-8; 6b, 78683-33-7; 7, 76207-09-5; 8, 76207-10-8; 8a, 82293-72-9; 8b, 82311-89-5; 8c, 82293-73-0; 9, 76207-11-9; 10, 76207-12-0; 11, 82293-74-1; 12, 82293-75-2; 13, 82293-76-3; LuCl_3 , 10099-66-8; NaC_5H_5 , 4984-82-1; $\text{LiCH}_2\text{Si}(\text{CH}_3)_3$, 1822-00-0; $\text{LiCH}_2\text{C}_6\text{H}_5$, 766-04-1; $\text{NaC}(\text{C}_6\text{H}_5)_3$, 4303-71-3; SnCl_3 , 10361-82-7; $(\text{C}_5\text{H}_5)_2\text{ErCl}$, 53224-35-4; $\text{LiC}(\text{CH}_3)_3$, 594-19-4; $(\text{C}_6\text{H}_5)_2\text{YbCl}$, 42612-73-7; methyl lithium, 917-54-4; ethyllithium, 811-49-4; isopropyllithium, 1888-75-1; butyllithium, 409-72-8; neopentyllithium, 7412-67-1; *p*-tolyllithium, 2417-95-0.

Supplementary Material Available: Tables of thermal parameters, calculated hydrogen atom positions, and additional non-lutetium bond distances and angles for compounds 8 and 10 as well as tables of observed and calculated structure factors (55 pages). Ordering information is given on any current masthead page.

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An X-ray Photoelectron Spectroscopy Study of Transition Metal μ -Methylene Complexes and Related Compounds

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Gas-phase core electron binding energies have been determined for $[\text{Fe}(\text{CO})_4]_2\text{CH}_2$, $[\text{CpMn}(\text{CO})_2]_2\text{CH}_2$, $(\text{CpCoCO})_2\text{CH}_2$, $(\text{CpRhCO})_2\text{CH}_2$, and several structurally related compounds. The binding-energy data indicate that the CH₂ groups in the μ -CH₂ complexes are highly negatively charged, especially in the manganese, cobalt and rhodium compounds. Data for $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ indicate that the CH₂ groups in this compound are negatively charged but less so than in the μ -CH₂ compounds. Data for $\text{Fe}_3(\text{CO})_{12}$ suggest the presence of both terminal and bridging carbonyl groups.

Introduction

In recent years several μ -methylene transition metal complexes have been prepared.²⁻⁸ These molecules are

of more than usual interest because they are analogs of methylene groups adsorbed on metal surfaces in heterogeneous catalysis and thus they may give information about important but poorly understood processes such as

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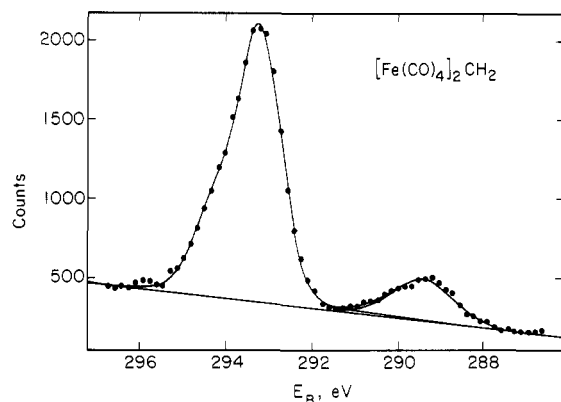
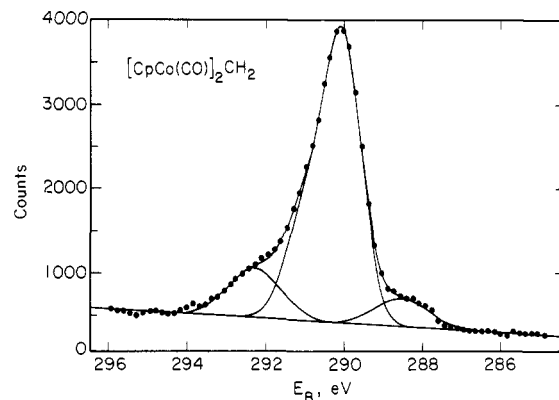
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Table I. Core Binding Energies (eV) of μ -Methylene Compounds and Comparison Compounds

compd	C 1s		O 1s		M core ^a	
	E_B	fwhm ^b	E_B	fwhm	E_B	fwhm
[CpMn(CO) ₂] ₂ CH ₂	288.6 (2) ^c	1.29 (20) CH ₂	538.40 (15)	1.85 (50)	646.12 (9)	1.22 (22)
	290.33 (4)	1.39 (12) Cp				
	291.87 (10)	1.29 (16) CO				
CpMn(CO) ₃ ^d	290.85 (3)	1.97 (7) Cp	538.90 (5)	1.45 (12)	646.72 (3)	1.35 (8)
	292.30 (7)	1.39 (12) CO				
[Fe(CO) ₄] ₃	293.32 (6)	1.55 (13)	539.52 (3) ^e	1.80 (11)	714.99 (3)	1.40 (9)
[Fe(CO) ₄] ₂ CH ₂	289.37 (6)	1.64 (15) CH ₂	539.69 (4)	1.54 (9)	715.14 (5)	1.19 (15)
	293.42 (3)	1.46 (7) CO				
Fe(CO) ₄ C ₂ H ₄	290.22 (5)	1.77 (14) C ₂ H ₄				
Fe(CO) ₅ ^f	293.71 (5)	1.27 (13)	539.96 (2)	1.38 (5)	715.79 (4)	1.25 (9)
(CpCoCO) ₂ CH ₂	288.46 (8)	1.56 (20) CH ₂	538.59 (6)	1.63 (16)	785.32 (5)	1.27 (16)
	290.23 (2)	1.45 (4) Cp				
	292.23 (9)	1.56 (11) CO				
CpCo(CO) ₂	290.67 (6)	1.49 (9) Cp	539.01 (7)	1.62 (11)	786.25 (7)	1.43 (14)
	292.68 (16)	2.00 (22) CO				
(CpRhCO) ₂ CH ₂	288.77 (9)	1.31 (20) CH ₂	538.79 (7)	1.62 (19)	314.28 (6)	1.47 (15)
	290.29 (2)	1.56 (4) Cp				
	292.38 (8)	1.31 (11) CO				
c-C ₃ H ₆ ^g	290.6					
(CH ₃) ₃ PCH ₂ ^h	288.00	CH ₂				

^a 3d_{5/2} for Rh; 2p_{3/2} for all others. ^b Full-width at half-maximum. ^c Uncertainty in last digit indicated parenthetically. ^d Data from: Chen, H. W.; Jolly, W. L.; Xiang, S. F.; Butler, I. S.; Sedman, J. J. *Electron Spectrosc. Relat. Phenom.* 1981, 24, 121. ^e Deconvolutable into peaks for bridging and terminal CO groups. See text. ^f Reference 24. ^g Reference 9. ^h Corrected datum from ref 17.

Figure 1. Carbon 1s spectrum of [Fe(CO)₄]₂CH₂.Figure 2. Carbon 1s spectrum of (CpCoCO)₂CH₂.

the Fischer-Tropsch process.⁴ To obtain information about the electron density (and hence about the chemical reactivity) of the methylene groups in these compounds, we have obtained gas-phase X-ray photoelectron spectra of four of these μ -methylene compounds: [CpMn(CO)₂]₂CH₂, [Fe(CO)₄]₂CH₂, (CpCoCO)₂CH₂, and (CpRhCO)₂CH₂. Each of these compounds contains a three-membered ring of the type



and may be looked upon as one member of a series of four three-membered ring compounds ranging from cyclopropane to a trinuclear metal complex. The binding energy of cyclopropane has been previously determined.⁹ We obtained the XPS spectra of Fe₃(CO)₁₂ and Fe(CO)₄C₂H₄ to complete the ferracyclopropane series and to help us interpret the data for the μ -methylene compounds.

Results and Discussion

Illustrative spectra are shown in Figures 1 and 2. Figure 1 shows the carbon 1s spectrum of [Fe(CO)₄]₂CH₂; the main peak is due to the eight CO groups, and the weak

peak at lower binding energy is due to the CH₂ group. Figure 2 shows the carbon 1s spectrum of (CpCoCO)₂CH₂; the spectrum has been deconvoluted into peaks for the two cyclopentadienyl groups, the two CO groups, and the CH₂ group.

The core binding energies of the μ -methylene complexes and related compounds are listed in Table I. Perhaps the most significant feature of the data is that the carbon 1s binding energies of the μ -CH₂ groups are very low. Even the highest μ -CH₂ binding energy, that of [Fe(CO)₄]₂CH₂, is 1.2 eV below the C 1s binding energy of cyclopropane, and the lowest, that of (CpCoCO)₂CH₂, is almost as low as the C 1s binding energy of the CH₂ group in (CH₃)₃PCH₂ (the latter binding energy is the lowest C 1s binding energy ever measured for a gaseous compound).

These data suggest that the μ -CH₂ groups in the dinuclear complexes are highly negatively charged, in agreement with extended Hückel calculations¹⁰ on (CpRhCO)₂CH₂ and CNDO¹¹ and Fenske-Hall¹² calculations on [CpMn(CO)₂]₂CH₂. However, one must be cautious in the interpretation of atomic core binding energy

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Table II. Calculated Charges on CH₂ Groups, from C 1s Binding Energies and the Potential Equation

compd	charge on CH ₂ group		
	using ΔE_R	using $(1/2)\Delta E_R$	assuming $\Delta E_R = 0$
[Fe(CO) ₄] ₂ CH ₂	-0.53	-0.62	-0.71
Fe(CO) ₄ C ₂ H ₄	-0.12	-0.18	-0.23

shifts when the nature of the attached groups changes as markedly as in these cases. On going from cyclopropane to [Fe(CO)₄]₂CH₂, the two groups attached to the methylene carbon atom change from CH₂ groups to Fe(CO)₄ groups. One might well suspect, because of the greater polarizability of the Fe(CO)₄ groups, that the electronic relaxation energy associated with the C 1s ionization of the CH₂ group is considerably greater in [Fe(CO)₄]₂CH₂ and Fe(CO)₄C₂H₄ than in cyclopropane and that a large part of the decrease in the CH₂ binding energy on going from cyclopropane to the iron complexes is due to the increase in relaxation energy. To obtain at least qualitative information regarding the actual charges on the CH₂ groups in these compounds, we have analyzed the CH₂ carbon binding energy shifts by using the "potential equation."¹³

Using the Potential Equation. The change in charge of the CH₂ carbon atom (ΔQ_C) on going from cyclopropane to [Fe(CO)₄]₂CH₂ or Fe(CO)₄C₂H₄ was calculated by using

$$\Delta E_B = k\Delta Q_C + \Delta V - \Delta E_R$$

where ΔE_B is the change in the CH₂ carbon 1s binding energy, k is 22.1 eV/charge,¹⁴ ΔV is the change in potential due to the charges of the other atoms, and ΔE_R is the change in relaxation energy. Relaxation energies were calculated by the "transition-state" method,¹⁵ using the equivalent cores approximation.¹⁶ The E_R values were calculated from the relation $E_R = 0.5[\Phi_{\text{val}}(\text{C}) - \Phi_{\text{val}}(\text{N}^+)]$, where $\Phi_{\text{val}}(\text{C})$ is the valence potential in the ground-state molecule and $\Phi_{\text{val}}(\text{N}^+)$ is the valence potential in the ion, approximated by replacing the C nucleus by the N nucleus.^{17,18} CNDO/2 wave functions¹⁹ were used for calculating E_R values, but CNDO/2 charges were not otherwise used in the solution of the potential equation. We assumed that the relative valence electron populations of the atoms in the Fe(CO)₄ groups are the same as calculated for Fe(CO)₅,^{20,21} that $Q_C = -0.1$ in cyclopropane,²² and that $\Delta Q_H/\Delta Q_C = 0.2$.²³ The experimental geometry of C₃H₆²⁴ was used, and symmetric idealized geometries

for [Fe(CO)₄]₂CH₂²⁵ (with no bridging CO groups) and Fe(CO)₄C₂H₄²⁶ were assumed. The C-H distances in the iron complexes were assumed to be the same as in cyclopropane. The calculated relaxation energies for cyclopropane, Fe(CO)₄C₂H₄, and [Fe(CO)₄]₂CH₂ are 17.00, 19.26, and 19.62 eV, respectively.

In Table II we present, for comparison, the calculated CH₂ group charges corresponding to the estimated relaxation energies, half of the estimated relaxation energies, and relaxation energies of zero. A correction factor of about half in conjunction with CNDO-estimated relaxation energies was found to give satisfactory correlations of binding energies in earlier studies,^{17,18} and such corrected relaxation energies are probably appropriate for this system.

The question arises, of course, as to how sensitive the calculated charges of the CH₂ groups are to the nature of the assumptions made in the calculations. We believe that the data in Table II show that any reasonable assumption regarding relaxation energy leads to the conclusion that the CH₂ group of [Fe(CO)₄]₂CH₂ possesses a substantial negative charge. The only other assumption which is both significant and disputable is the assumption that the relative valence electron populations of the atoms in the Fe(CO)₄ groups are the same as obtained in an ab initio calculation for Fe(CO)₅ (for which the Fe, C, and O atomic charges were calculated to be 1.039, 0.174, and -0.381, respectively). If we arbitrarily assume that the Fe, C, and O atoms of Fe(CO)₅ have the drastically different charges of 0.5, 0.15, and -0.25, respectively, the calculations give CH₂ charges of -0.36 (using 1/2 ΔE_R) and -0.27 (using ΔE_R). Clearly our calculation of a substantial negative charge for the CH₂ group is not the result of an unreasonable assumption regarding the other atomic charges. Taking account of the various uncertainties in the calculations, we conclude that the charges on the CH₂ groups in [Fe(CO)₄]₂CH₂ and Fe(CO)₄C₂H₄ are -0.5 ± 0.2 and -0.2 ± 0.1 , respectively.

Other Data. Our calculated charges for the CH₂ groups in Fe(CO)₄C₂H₄ and [Fe(CO)₄]₂CH₂ are qualitatively consistent with Vites and Fehlner's²⁷ interpretation of the UPS spectrum of [Fe(CO)₄]₂CH₂ (that the CH₂ group is negatively charged) and Oskam et al.'s²⁸ interpretation of the UPS spectrum of Fe(CO)₄C₂H₄ (that the C₂H₄ group is only slightly negative). It is also significant that Calabro and Lichtenberger²⁹ recently concluded, on the basis of extended Hückel and Fenske-Hall calculations, that there is no significant overall charge transfer between the metal and olefin in CH₃CpMn(CO)₂C₂H₄, although they did conclude¹² that the CH₂ group in [CpMn(CO)₂]₂CH₂ has a high negative charge.

Because the CH₂ carbon binding energy of [Fe(CO)₄]₂CH₂ is much higher than that of any of the other μ -CH₂ compounds in Table I, it is clear that the CH₂ groups in the other μ -CH₂ compounds are even more negatively charged. Very high negative charges on the CH₂ groups of (CpCoCO)₂CH₂ and (CpRhCO)₂CH₂ are consistent with experimental indications that these compounds can be protonated to form the corresponding μ -CH₃ cations.^{3c,6b}

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The C 1s and O 1s binding energies of the CO groups as well as the C 1s binding energy of the CH₂ group are lower in (CpCoCO)₂CH₂ than in [Fe(CO)₄]₂CH₂. These data indicate that the effective valence electron density, or "electron pressure", on the cobalt atom is greater than that on the iron atom, a result which is readily explained by the fact that the iron atom is attached to four strongly electron-withdrawing carbonyl groups, whereas the cobalt atom is attached to only one such group. The μ -CH₂ binding energies of (CpCoCO)₂CH₂ and [CpMn(CO)₂]₂CH₂ are the same, within experimental error. It appears that, on going from the cobalt compound to the manganese compound, the decrease in the electronegativity of the metal compensates for the small increase in the number of carbonyl groups.

The metal, carbon, and oxygen binding energies of CpMn(CO)₃, Fe(CO)₅, and CpCo(CO)₂ are higher than the corresponding binding energies of [CpMn(CO)₂]₂CH₂, [Fe(CO)₄]₂CH₂, and (CpCoCO)₂CH₂. These differences are not unexpected. The carbonyl group is known to be a very strong electron-withdrawing ligand, and it would be surprising if a CH₂ group could withdraw as much electron density from two CpMn(CO)₂, Fe(CO)₄, or CpCoCO groups as a CO group withdraws from one such group. Thus the CpMn(CO)₃, Fe(CO)₅, and CpCo(CO)₂ data are consistent with substantial negative charges on the μ -CH₂ groups.

All the core binding energies of Fe₃(CO)₁₂ are significantly lower than the corresponding binding energies of [Fe(CO)₄]₂CH₂. This result probably has two causes. First, because of the negative charge on the CH₂ group, the iron atoms and CO groups of [Fe(CO)₄]₂CH₂ are more positively charged than in Fe₃(CO)₁₂. Second, probably two of the CO groups of Fe₃(CO)₁₂ are bridging (as in the solid state³⁰). Hence the iron, carbon and oxygen average binding energies are lower than they would be in the case of a nonbridged structure.^{31,32} The C 1s spectrum of Fe₃(CO)₁₂ consists of only one peak with a not overly large fwhm (1.55 eV). However the O 1s spectrum consists of a rather broad band (fwhm = 1.80 eV) with a hump on the low binding energy side which can be deconvoluted into two peaks of 5:1 intensity ratio (at 539.66 and 538.5 eV,

respectively), corresponding to terminal and bridging CO groups.

Experimental Section

Vapor-phase X-ray photoelectron spectra were obtained by using procedures described previously.^{32,33}

The (ethylene)iron tetracarbonyl was prepared by the method of Murdoch and Weiss.³⁴ Even after repeated fractional condensation on the vacuum line, the product was highly contaminated with Fe(CO)₅, which has a volatility similar to that of Fe(CO)₄C₂H₄. The vapor-phase infrared spectrum corresponded to a mixture of Fe(CO)₅ and Fe(CO)₄C₂H₄, with no free ethylene.^{35,36} Immediately before running the C 1s spectrum of the sample, it was held at -78 °C under high vacuum to remove any possible free ethylene. The spectrum was then obtained while the sample was held at -15 °C. The spectrum consisted of a peak around 293.7 eV (due to the CO groups of the Fe(CO)₅ and Fe(CO)₄C₂H₄) and a peak at 290.22 eV (relative intensity 0.23) due to the coordinated C₂H₄. In Table I we have reported the binding energy only of the latter peak. The relative peak intensities did not change significantly during the run.

The (CpCoCO)₂CH₂ was prepared from Na[CpCoCO]₂ (synthesized as described by Schore et al.³⁷) and CH₂I₂, as summarized in a recent communication.^{6b} Additional details of the synthesis and properties of this material will be reported in a full paper.³⁸

The [CpMn(CO)₂]₂CH₂ and (CpRhCO)₂CH₂ were prepared and characterized by procedures previously described.^{3a-c} The samples were purified by low-temperature recrystallization from *n*-pentane/diethyl ether solutions.

The spectrometer was held at 50 °C for Fe₃(CO)₁₂ and [Fe(CO)₄]₂CH₂, 52 °C for (CpCoCO)₂CH₂, and 65 °C for (CpRhCO)₂CH₂ and [CpMn(CO)₂]₂CH₂ in order to generate sample vapor pressures high enough to give satisfactory spectra.

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Registry No. [CpMn(CO)₂]₂CH₂, 57603-41-5; CpMn(CO)₃, 12079-65-1; [Fe(CO)₄]₃, 17685-52-8; [Fe(CO)₄]₂CH₂, 73448-09-6; Fe(CO)₄C₂H₄, 32799-25-0; Fe(CO)₅, 13463-40-6; (CpCo(O)₂)₂CH₂, 77674-08-9; CpCo(CO)₂, 12078-25-0; (CpRhCO)₂CH₂, 62154-28-3.

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