

- (5) The calculated absorption coefficient for Mo K α radiation is $\mu = 25.8 \text{ cm}^{-1}$.
- (6) The original structural study of $\text{Os}_3(\text{CO})_{12}$,⁷ was based on space group $P2_1/n$ as was our redetermination of this structure.¹ The determination of $\text{Ru}_3(\text{CO})_{12}$ by Mason and Rae² was based upon space group $P2_1/c$; our redetermination of this structure is based instead upon space group $P2_1/n$ so all results will be directly comparable with those obtained on $\text{Os}_3(\text{CO})_{12}$. The structures of $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ are isomorphous.
- (7) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).
- (8) $R_F = 100 \sum (|F_o| - |F_c|) / \sum |F_o|$; $R_w F = 100 [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (n - m)]^{1/2}$, where n is the number of reflections and m is the number of variables.
- (9) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963); see also G. H. Stout and L. H. Jensen, "X-Ray Structure Determination", Macmillan, London, 1968, pp 411-412, especially eq 17.16.
- (10) "International Tables for X-Ray Crystallography", Vol. 4, Kynoch Press, Birmingham, England, 1974: (a) Table 2.2B, pp 99-101; (b) Table 2.3.1, pp 149-150.

Contribution from the Department of Chemistry, University of California, and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720, the Department of Chemistry, University of Western Ontario, London, Ontario N6A 3K7, Canada, and the Institute of Physics, S-751 21 Uppsala, Sweden

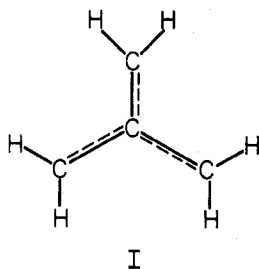
ESCA Spectra of Trimethylenemethaneiron Tricarbonyl and Butadieneiron Tricarbonyl

J. W. Koepke,^{1a} W. L. Jolly,^{*1a} G. M. Bancroft,^{1b}
P. Å. Malmquist,^{1c} and K. Siegbahn^{1c}

Received February 9, 1977

AIC70107K

The trimethylenemethane diradical (I) has been the subject



of considerable theoretical speculation.^{2,3} It has been detected only at low concentrations as an unstable intermediate.^{3a} An ab initio calculation by Yarkony and Schaefer⁴ indicated that the central carbon has a charge of +0.62, comparable to the charge of the carbon atom in CHF_3 . Although trimethylenemethane itself is too unstable to allow investigation of its charge distribution by ESCA, we have studied the ESCA spectrum of the relatively stable complex trimethylenemethaneiron tricarbonyl.⁵ For comparison we have also studied the structural isomer butadieneiron tricarbonyl.

Savariaut and Labarre⁶ reported, on the basis of CNDO/2 calculations, that the bonds between the iron atom and the three CH_2 groups of trimethylenemethaneiron tricarbonyl are much stronger than the bond between the iron atom and the central carbon. They calculated atomic charges of +0.67 for the iron atom, +0.09 for the carbonyl carbon atoms, -0.30 for the CH_2 carbon atoms, and +0.17 for the central carbon atom and explained the weak bond between the iron atom and the central carbon atom in terms of electrostatic repulsion. We hoped that measurement of the carbon 1s binding energies of the compound would give enough information regarding the charge distribution in the molecule to test these calculations.

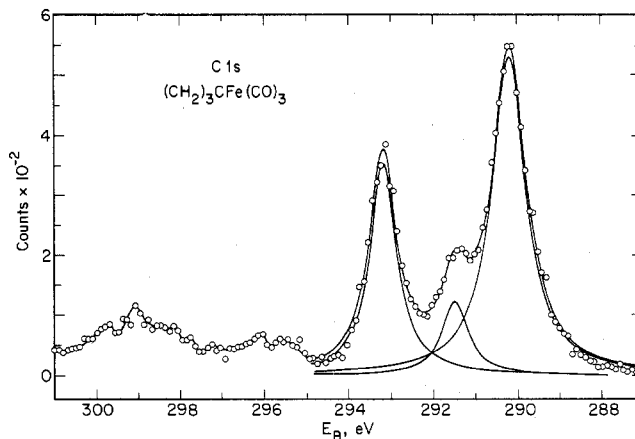


Figure 1. Carbon 1s spectrum of trimethylenemethaneiron tricarbonyl, deconvoluted using Lorentzian curves. The relative intensities of the three peaks are 2.96:1:5.72.

Trimethylenemethane has been implicated as an intermediate in several reactions,⁷ and our results will determine whether ESCA can serve as a tool to search for trimethylenemethane intermediates on catalyst surfaces.

Experimental Section

Butadieneiron tricarbonyl was prepared as described by King⁸ and was identified by its infrared spectrum⁹ and NMR spectrum. Trimethylenemethaneiron tricarbonyl was prepared by the reaction of 3-chloro-2-methylpropene with $\text{Fe}_2(\text{CO})_9$.⁵ Both the IR and NMR spectra were consistent with the literature.⁵

Both ESCA spectra were obtained in the gas phase. The spectrum of trimethylenemethaneiron tricarbonyl was recorded on the Uppsala electrostatic high-resolution spectrometer.¹⁰ The C 1s and O 1s lines of carbon monoxide were used as references. We used 296.22 and 542.57 eV for the C 1s and O 1s binding energies of CO, respectively; these are averages of the values obtained by Smith and Thomas¹¹ and Perry and Jolly.¹² The Fe $2p_{3/2}$ binding energy of trimethylenemethaneiron tricarbonyl was measured relative to the F 1s binding energy of CF_4 , using 695.55 eV for the latter binding energy (an average of literature values^{13,14}). The reference gases and sample vapors were run simultaneously. The spectrum of butadieneiron tricarbonyl was recorded on the old Berkeley magnetic spectrometer.¹⁵ Argon was introduced with the sample, and the Ar $2p_{3/2}$ line ($E_B = 248.62 \text{ eV}$)¹⁶ was used as a reference for all lines of butadieneiron tricarbonyl. Sample and reference lines were scanned alternately. The best least-squares fitting of the data was obtained assuming Lorentzian curves in the case of trimethylenemethaneiron tricarbonyl and Gaussian curves in the case of butadieneiron tricarbonyl.

Results and Discussion

The C 1s spectra are shown in Figures 1 and 2, and Table I lists all the binding energies. The smaller line widths obtained for trimethylenemethaneiron tricarbonyl reflect the better resolution of the Uppsala instrument. The peaks are easily assigned by comparison with the binding energies of other organometallic compounds and by intensity considerations. The peaks at 293.17 eV in Figure 1 and at 293.03 eV in Figure 2 are in the region typical of metal carbonyls and can be confidently assigned to the CO groups in the compounds. In Figure 1, the relatively weak peak at 291.47 eV is undoubtedly due to the central carbon, and the 290.18-eV peak is due to the CH_2 groups. The CO peaks in both spectra and the central carbon peak in Figure 1 have lost considerable intensity to shake up bands at higher energy. In the case of butadieneiron tricarbonyl our results can be compared with those of Connor et al.,¹⁷ who obtained an ESCA spectrum of this compound in the gas phase. Their reported C 1s and O 1s binding energies are 0.3-0.4 eV higher than ours, whereas their Fe $2p_{3/2}$ value is essentially the same as ours. The discrepancies are not unreasonable in view of their estimated accuracy of $\pm 0.2 \text{ eV}$. The intensity ratio of the C 1s peaks due to the CO

Table 1. Experimental Binding Energies

Compd	Binding energies, eV					
	C 1s ^a	Fwhm	O 1s ^a	Fwhm	Fe 2p _{3/2} ^a	Fwhm
Butadieneiron tricarbonyl	290.62 (3) (C ₄ H ₆)	1.98	539.29 (4)	1.31	714.84 (4)	1.21
Trimethylenemethaneiron tricarbonyl	290.18 (2) (CH ₂)	0.78	539.36 (5)	0.80	715.14 (4)	1.33
	291.47 (5) (C)	0.82				
	293.17 (2) (CO)	0.67				

^a The probable uncertainty in the last digit, as determined by the least-squares curve fitting, is parenthesized.

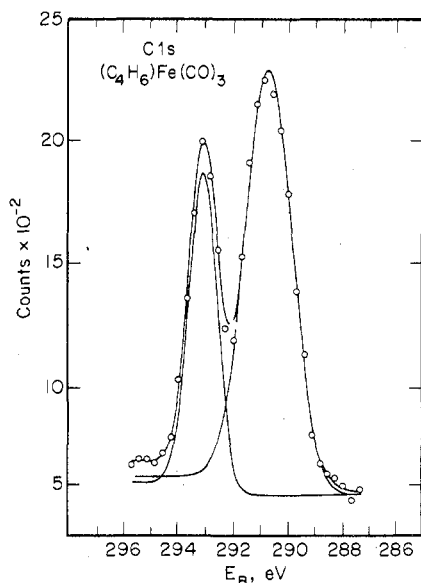
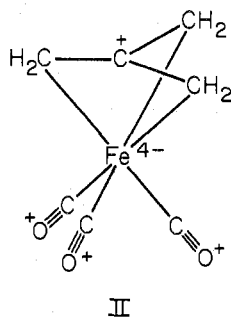


Figure 2. Carbon 1s spectrum of butadieneiron carbonyl, deconvoluted using Gaussian curves. The relative intensities of the peaks are 1:2.16.

and butadiene ligands would be 1:1.33, respectively, if the intensities were proportional to the atom abundances. Connor et al. measured an intensity ratio of 1:1.11 for these peaks. In contrast, the value which we measured for this ratio (1:2.16) indicates, as one might expect, more shake-up associated with the CO ionization than the butadiene ionization.

A very simple interpretation of the C 1s binding energies (ignoring relaxation energies) would put the charge of the central carbon atom of the trimethylenemethane group between those of the CO carbon atoms and the CH₂ carbon atoms. This charge distribution is not at all consistent with the calculations of Savariault and Labarre. However, by taking account of relaxation energies, we can show that the data are consistent with a very positively charged central carbon atom in the trimethylenemethane group. The bonding in trimethylenemethaneiron tricarbonyl can be crudely represented by valence bond structure II. This structure is

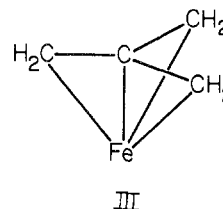


somewhat misleading because it does not show any back-bonding to the three carbonyl groups. However the representation of the bonding to the trimethylenemethane group, which also shows no back-bonding, is probably reasonably

accurate, in view of the fact that back-bonding to carbonyl groups is generally recognized to be much greater than that to olefins and other unsaturated organic ligands. The core ionization of a ligand atom causes an increase in the amount of back-bonding to the ligand if the back-bonding effects a shift of negative formal charge to the core-ionized atom. This increase in the degree of back-bonding corresponds to an extraordinarily large relaxation energy associated with the core ionization and causes the binding energy associated with the core ionization to be lower than otherwise expected. In many nonmetal carbonyl compounds, π donation from neighboring groups can cause a decrease in the formal charge of the oxygen atom, but no change in the formal charge of the carbon atom:



Hence in such compounds "extra" relaxation energy (as much as 3 eV) due to π -donor relaxation has been detected in the oxygen 1s ionizations, whereas the carbon 1s ionizations are normal.¹⁸ Similar results have been obtained for transition metal carbonyls.¹⁹ Now let us consider the trimethylenemethane group, in view of these facts. Back-bonding to this group can be represented by structure III, in which negative



formal charge has been transferred from the iron atom to the central carbon atom. There is no change in the formal charges of the CH₂ carbon atoms (at least this is so if structure II is accepted as the non-back-bonded structure); hence one expects no extraordinarily large relaxation energy associated with the CH₂ C 1s ionization. On the other hand, one expects an extraordinarily large relaxation energy in the C 1s ionization of the central carbon atom. In other words, the binding energy of the central carbon atom is lower than would be expected on the basis of its ground-state charge. Thus the C 1s spectrum is consistent with a high positive charge on the central carbon atom, possibly higher than that of the carbonyl carbon atoms.

It is significant that the weighted average of the CH₂ carbon and central carbon binding energies of trimethylenemethaneiron tricarbonyl is 290.50 eV, close to the 290.62-eV binding energy of the carbon atoms in the butadiene group of butadieneiron tricarbonyl. This result suggests that the overall donor and acceptor characters of trimethylenemethane and butadiene are similar and that the relaxation energy associated with the butadiene ligand (in which each carbon atom has a formal charge of +¹/₄ in the non-back-bonded ground-state molecule) is close to the weighted average of the relaxation energies of the trimethylenemethane ligand. Indeed, Dewar and Worley concluded,²⁰ on the basis of the ultraviolet photoelectron spectra of these same complexes,^{20,21} that the perturbation by Fe(CO)₃ of the π molecular orbitals of bu-

tadiene and trimethylenemethane are similar.

However, the fact that the weighted average of the C 1s binding energies of the trimethylenemethane ligand is actually slightly less than the C 1s binding energy of the butadiene ligand suggests slightly greater back-bonding to trimethylenemethane than to butadiene. This interpretation is consistent with the fact that the Fe 2p_{3/2}, carbonyl C 1s, and O 1s binding energies are higher (by 0.30, 0.14, and 0.07 eV, respectively) in the trimethylenemethane complex than in the butadiene complex. Indeed, even infrared C–O stretching frequencies indicate more back-bonding to the trimethylenemethane ligand than to the butadiene ligand.²²

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE73-05133 A02) and the U.S. Energy Research and Development Administration. We wish to thank Mr. Tom Webb for preparation of butadieneiron tricarbonyl.

Registry No. (CH₂)₃CFe(CO)₃, 12078-33-0; (C₄H₆)Fe(CO)₃, 12078-32-9.

References and Notes

- (1) (a) University of California and Lawrence Berkeley Laboratory. (b) University of Western Ontario. (c) Institute of Physics, Uppsala.
- (2) For early discussions, see the citations in ref 3.
- (3) (a) P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966); (b) R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966).
- (4) D. R. Yarkony and H. F. Schaefer, *J. Am. Chem. Soc.*, **96**, 3754 (1974).
- (5) K. Ehrlich and G. F. Emerson, *J. Am. Chem. Soc.*, **94**, 2464 (1972).
- (6) J.-M. Savariault and J.-F. Labarre, *Inorg. Chim. Acta*, **19**, L53 (1976).
- (7) F. Weiss, *Q. Rev. Chem. Soc.*, **24**, 278 (1970).
- (8) R. B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York, N.Y., 1965, pp 128–129.
- (9) B. F. Hallam and P. F. Pauson, *J. Chem. Soc.*, 642 (1958).
- (10) U. Gelius, E. Basilier, S. Svensson, T. Bergmark, and K. Siegbahn, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 405 (1973).
- (11) S. R. Smith and T. D. Thomas, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 45 (1976).
- (12) W. B. Perry and W. L. Jolly, unpublished work.
- (13) T. D. Thomas and R. W. Shaw, *J. Electron Spectrosc. Relat. Phenom.*, **5**, 1081 (1974).
- (14) W. Perry and W. L. Jolly, *Inorg. Chem.*, **13**, 1211 (1974). The value used differs from the published value because of the use of the value 248.62 eV for the Ar 2p_{3/2} reference.
- (15) J. M. Hollander, M. D. Holtz, T. Novakov, and R. L. Graham, *Ark. Fys.*, **28**, 375 (1965).
- (16) G. Johansson, J. Hedman, A. Berndtsson, M. Klasson, and R. Nilsson, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 295 (1973).
- (17) J. A. Connor, L. M. R. Derrick, M. B. Hall, I. H. Hillier, M. F. Guest, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, **28**, 1193 (1974).
- (18) W. L. Jolly and T. F. Schaaf, *J. Am. Chem. Soc.*, **98**, 3178 (1976).
- (19) W. L. Jolly, S. C. Avanzino, and R. R. Rietz, *Inorg. Chem.*, **16**, 964 (1977).
- (20) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **51**, 1672 (1969).
- (21) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).
- (22) D. C. Andrews and G. Davidson, *J. Organomet. Chem.*, **43**, 393 (1972).

Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

Trans Group 6 Metal Dicarboxyls. Stereochemical Control by Seven-Coordinate Intermediates

S. Datta, T. J. McNeese, and S. S. Wreford*

Received April 17, 1977

AIC70275C

Associative substitution reactions of four-coordinate species which proceed stereospecifically because of the nature of the five-coordinate intermediate or transition state are well established.¹ Several examples of similar stereochemical control in dissociative substitution reactions of octahedral species are also available.² In principle, the geometric and site preferences of a seven-coordinate intermediate or transition state should

be capable of determining the overall stereochemistry of associative substitution reactions. However, no such examples are explicitly known.

The group 6 dicarbonyls of the general formula M(CO)₂(L-L)₂ (L-L = bidentate phosphine or arsine) generally exist as the thermodynamically favored *cis* isomers,³ with the exception of the chromium complexes Cr(CO)₂[o-C₆H₄(PETe)₂]₂ and Cr(CO)₂[C₂H₄(PPh₂)₂]₂, which exhibit *cis*–*trans* isomerism.⁴ In contrast, the analogous seven-coordinate hydrides, [MH(CO)₂(L-L)₂]⁺, possess a monocapped octahedral structure, in which the carbonyls are mutually *trans*.^{5,6} We report a simple preparation of metastable *trans*-M(CO)₂(L-L)₂ utilizing the stereochemistry of the seven-coordinate hydride as a controlling factor.

Experimental Section

Solvents were purified by distillation from sodium benzophenone ketyl except for *tert*-butyl alcohol, which was distilled from sodium. *cis*-Mo(CO)₂(dmpe)₂,^{5a,7} *cis*-Mo(CO)₂(diphos)₂,³ *cis*-Mo(CO)₂(diars)₂,⁸ and *cis*-W(CO)₂(dmpe)₂^{5a} were prepared by literature methods.⁹

All reactions were performed under an atmosphere of prepurified nitrogen. Infrared, 100-MHz ¹H and 40.5-MHz ³¹P NMR, and mass spectra were obtained on Perkin-Elmer 457A, Varian XL-100, and AEI MS-9 spectrometers, respectively. ³¹P NMR chemical shifts are relative to external 85% phosphoric acid. Elemental analyses were by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

[MoH(CO)₂(diphos)₂][SO₃F] (1). HSO₃F (39 μL, 0.68 mmol) was added via a syringe to 450 mg (0.47 mmol) of *cis*-Mo(CO)₂(diphos)₂ in 25 mL of tetrahydrofuran. The extent of the reaction was monitored by infrared spectroscopy and within minutes complete conversion to the hydride was achieved. The solvent was removed in vacuo leaving light pink crystals. Recrystallization from tetrahydrofuran afforded 400 mg of 1: ¹H NMR (acetone-*d*₆) τ 15.28 (triplet of triplets, J_{PAH} = 70.8, J_{PBH} = 14.0 Hz); ³¹P{¹H} NMR (acetone) 26.1 and 49.0 ppm (AA'BB' pattern); IR (THF solution) ν_{CO} 1873 cm⁻¹ (vs).

Anal. Calcd for C₅₄H₄₉FMoO₅P₄S: C, 61.84; H, 4.71. Found: C, 62.08; H, 4.87.

[MoH(CO)₂(dmpe)₂][SO₃F] (2). 2 was prepared analogously except that ether was used as the solvent: ¹H NMR (Me₂SO-*d*₆) τ 16.20 (triplet of triplets, J_{PAH} = 68.2, J_{PBH} = 8.6 Hz); ³¹P{¹H} NMR (acetone) 28.9 and 51.9 ppm (AA'BB' pattern); IR (THF solution) ν_{CO} 1868 cm⁻¹ (vs).

Anal. Calcd for C₁₄H₃₃FMoO₅P₄S: C, 30.45; H, 6.02. Found: C, 29.93; H, 5.50.

[MoH(CO)₂(diars)₂][SO₃F] (3). 3 was prepared analogously to 1: ¹H NMR (acetone-*d*₆) τ 15.52; IR (THF solution) 1879 cm⁻¹ (vs).

Anal. Calcd for C₂₂H₃₃As₄FMoO₅S: C, 32.06; H, 4.04. Found: C, 31.80; H, 3.88.

[WH(CO)₂(dmpe)₂][SO₃F] (4). 4 was prepared analogously to 1: ¹H{³¹P} NMR (acetone-*d*₆) τ 16.43; IR (THF solution) ν_{CO} 1852 cm⁻¹ (vs).

Anal. Calcd for C₁₄H₃₃FO₅P₄SW: C, 26.27; H, 5.20. Found: C, 26.81; H, 5.15.

trans-Mo(CO)₂(dmpe)₂. To 750 mg of 2 (1.36 mmol) suspended in 15 mL of THF at -78 °C was added 1.40 mL of a 1.00 M solution of potassium in *tert*-butyl alcohol. After warming of the mixture to 5 °C, 2 had completely dissolved, giving a bright yellow solution. After evaporation of the solvent at 5 °C, the residue was stirred with 30 mL of ether and 10 mL of pentane for 5 min at 25 °C. The solution was filtered and the filtrate concentrated at 0 °C to ca. 5 mL. Cooling to -78 °C gave yellow crystals which were collected by filtration, washed with 2 × 2 mL of pentane at -78 °C, and dried in vacuo at 25 °C. The resulting *trans*-Mo(CO)₂(dmpe)₂ was stored at -78 °C under N₂ (397 mg, 65%): ³¹P{¹H} NMR (benzene) 41.0 (s) ppm;¹⁰ IR (hexane solution) ν_{CO} 1815 (vs) cm⁻¹; mass spectrum *m/e* 452 P⁺, 424 [P – CO]⁺, and 396 [P – 2CO]⁺.

Anal. Calcd for C₁₄H₃₂MoO₂P₄: C, 37.18; H, 7.13. Found: C, 36.91; H, 7.29.

Similarly, addition of potassium *tert*-butoxide to 1, 3, or 4 at 0 °C in THF solution resulted in total disappearance of the ν_{CO} of the hydrides and formation of a single new band for the *trans* isomers: *trans*-Mo(CO)₂(diphos)₂, 1823 cm⁻¹; *trans*-Mo(CO)₂(diars)₂, 1818 cm⁻¹; *trans*-W(CO)₂(dmpe)₂, 1796 cm⁻¹. In each case, refluxing the solution resulted in disappearance of the band for the *trans* isomers