Photoelectron Spectra of some Compounds containing Transition-metal–Carbon σ-Bonds

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Photoelectron spectra of $[MMe(\eta\text{-}C_5H_5)(CO)_3]$ (M = Mo and W), $[MMe(\eta\text{-}C_5H_5)(CO)_2]$ (M = Fe and Ru), and $[Fe(CH_2CN)(\eta\text{-}C_5H_5)(CO)_2]$ have been measured. The ionization energies for the metal–carbon σ-bonding electrons are identified and compared with those of other transition-metal alkyl compounds.

IONIZATIONS associated with transition-metal–carbon σ bonds have been characterized for pure metal alkyls,[1,2] cyclopentadienylmetal alkyls,[3] and carbonylmetal alkyls.[4] A recent report [5] of the spectrum of $[FeMe(\eta\text{-}C_5H_5)(CO)_2]$ prompts us to report our study of this and related molecules.

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[1] S. Evans, J. C. Green, and S. E. Jackson, *J.C.S. Faraday II*, 1973, 191.

[2] L. Galyer, G. Wilkinson, and D. R. Lloyd, *J.C.S. Chem. Comm.*, 1975, 497.

[3] J. C. Green, S. E. Jackson, and B. Higginson, *J.C.S. Dalton*, 1975, 403.

[4] B. R. Higginson, D. R. Lloyd, S. Evans, and A. F. Orchard, *J.C.S. Faraday II*, 1975, 1913.

[5] D. A. Symon and T. C. Waddington, *J.C.S. Dalton*, 1975, 2140.

EXPERIMENTAL

Dicarbonyl(η-cyclopentadienyl)methyliron was prepared[6] from Na[Fe(η-C_5H_5)$(CO)_2$] and MeI, and purified by sublimation at 60 °C *in vacuo*. The mass spectrum showed a mixture of [FeMe(η-C_5H_5)$(CO)_2$] and [Fe(η-C_5H_5)$_2$], but the i.r. spectrum was identical with the published spectrum and showed no trace of ferrocene. The photoelectron (p.e.) spectrum was checked carefully for evidence of ferrocene, but none was found. The compound [FeMe(η-C_5H_5)$(CO)_2$] is known to decompose thermally to ferrocene below 110 °C. Dicarbonyl(η-cyclopentadienyl)methylruthenium was prepared[7] analogously by Dr. M. G. Swanick, and purified by sublimation at 40—50 °C *in vacuo*. Tricarbonyl(η-cyclopentadienyl)methylmolybdenum and its tungsten analogue were prepared[6] from Na[M(η-C_5H_5)$(CO)_3$] (M = Mo and W) and MeI. The yellow needle-shaped crystals were purified by sublimation at 50 °C *in vacuo*. Dicarbonyl(cyanomethyl)(η-cyclopentadienyl)iron was prepared[8] from Na[Fe(η-C_5H_5)$(CO)_2$] and $ClCH_2CN$ and purified by column chromatography and sublimation at 80 °C *in vacuo*. The mass spectrum showed no parent-ion peak, but there were peaks due to ferrocene. The i.r. spectrum agreed exactly with the published spectrum and showed no bands due to ferrocene. The p.e. spectrum also showed no evidence of ferrocene. This compound is known to decompose thermally to ferrocene, like its methyl analogue.

TABLE 1

Measurement conditions

Compound	Spectrometer	θ_c/°C	Counts/s^{-1}
[MoMe(η-C_5H_5)$(CO)_3$]	*a*	25	50
[WMe(η-C_5H_5)$(CO)_3$]	*a*	40	50
	b	60	10^4
[FeMe(η-C_5H_5)$(CO)_2$]	*a*	25	500
	b	20	10^4
[RuMe(η-C_5H_5)$(CO)_2$]	*c*	25	100
[Fe(CH_2CN)(η-C_5H_5)$(CO)_2$]	*a*	40	150

[a] See S. Evans, A. F. Orchard, and D. W. Turner, *Internat. J. Mass. Spectrometry Ion Phys.*, 1971, **7**, 261. [b] Perkin-Elmer PS 16/18. [c] D. W. Turner, *Proc. Roy. Soc.*, 1968, **A307**, 15.

The conditions for obtaining the p.e. spectra of these compounds are indicated in Table 1. The spectra were calibrated using rare gases and ionization energies obtained (Table 2) are accurate to ±0.1 eV.*

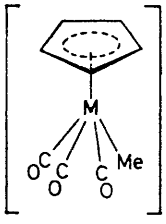
TABLE 2

Vertical ionization energies (eV)

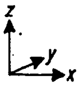
[MMe(η-C_5H_5)$(CO)_3$]		[MMe(η-C_5H_5)$(CO)_2$]			
Mo	W	Fe	Ru	[Fe(CH_2CN)(η-C_5H_5)$(CO)_2$]	Assignment
7.78	(7.6)	7.78	8.13	8.29	*d* orbitals
	7.77	8.53	8.29	8.90	
			8.96	9.48	
9.07	9.26	9.15	9.48	11.14	M–C
9.7	9.92	9.90	9.98	10.25	C_5H_5 e_1
10.0	10.2		10.51		
(12.2)	(12.3)	(12.1)			CH_3
				11.89	CN
				12.27	
13.8	13.3	13.4	13.0	13.2	C_5H_5
17.3	13.8	13.9		14.0	and CO
	17.3	17.3		14.6	
				17.7	

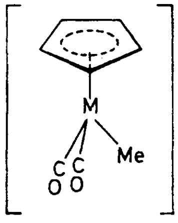
RESULTS AND DISCUSSION

The crystal structure of the compound [MoEt(η-C_5H_5)$(CO)_3$] has been determined by *X*-ray diffraction,[9] and the structures of [MMe(η-C_5H_5)$(CO)_3$] (M = Mo or W) are assumed to be similar to this (I). The crystal structure of [Fe(CH_2CO_2H)(η-C_5H_5)$(CO)_2$] has been determined by *X*-ray diffraction[10] and by analogy with this the assumed structures of [MMe(η-C_5H_5)$(CO)_2$] (M = Fe and Ru) are given in (II). Thus these molecules are assumed to have C_s symmetry. To construct molecular-orbital (m.o.) schemes for these molecules we used the ' molecules in molecules ' approach described previously.[3] The methyl group is added to the M(η-C_5H_5)$(CO)_n$ unit in C_s symmetry.



(I)





(II)

[MMe(η-C_5H_5)$(CO)_3$] (M = Mo *or* W).—A qualitative m.o. scheme for these compounds is given in Figure 1. The orbitals for the M(η-C_5H_5)$(CO)_3$ unit were derived by using the p_π orbitals of the C_5H_5 ring and the σ-donor and π*-acceptor orbitals of the CO ligands. Any other ligand orbitals were neglected. This scheme is substantiated by the p.e. spectrum of [Mn(η-C_5H_5)$(CO)_3$].[11] The 18 valence electrons fill the orbitals up to the level indicated.

The spectra of [MMe(η-C_5H_5)$(CO)_3$] (M = Mo and W) (see Figure 2) are strikingly similar, as expected for second- and third-row transition metals of this Group.[3] The bands at 7.78 (Mo) and 7.77 eV (W) are assigned to ionization from the metal *d* orbitals $6a'$ and $3a''$. The

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* 1 eV ≈ 1.6 × 10^{-19} J.

[6] T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

[7] M. G. Swanick, D.Phil. Thesis, Oxford, 1970.

[8] J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, 1963, 2976.

[9] M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 1963, 273.

[10] M. L. H. Green, J. K. P. Ariyaratne, A. M. Bierrum, M. Ishaq, and C. K. Prout, *Chem. Comm.*, 1967, 430.

[11] S. E. Jackson, D.Phil. Thesis, Oxford, 1973.

band of the tungsten compound showed a shoulder at 7.60 eV, absent in the molybdenum analogue, indicating a slightly increased *d*-orbital splitting for the heavier element. The first band in the spectrum of the tungsten compound was relatively more intense than the first band in the spectrum of the molybdenum compound, in line with other observations of increasing ionization cross-section with atomic number.[4]

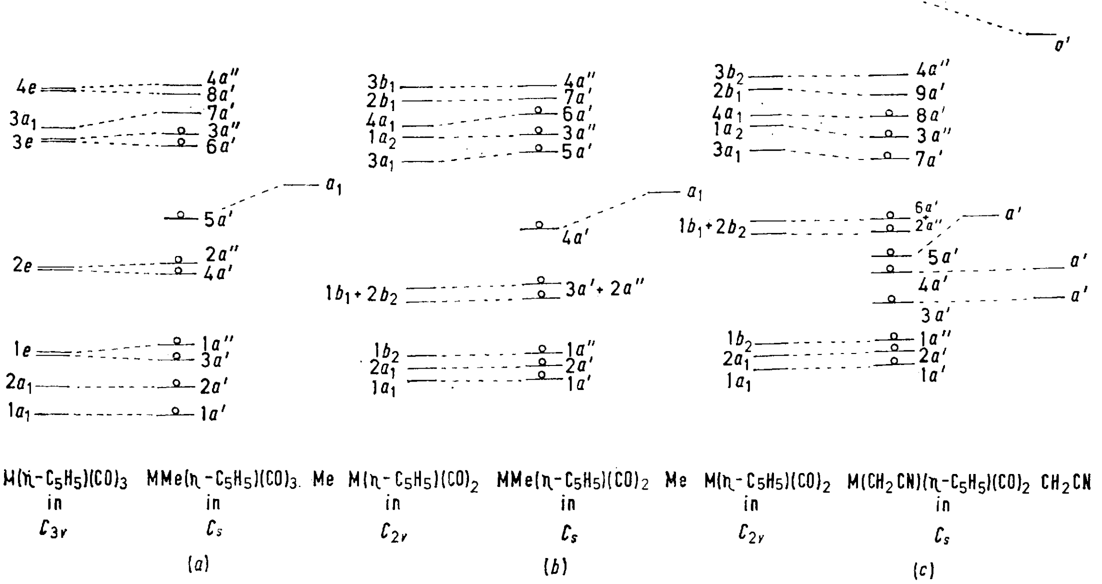

FIGURE 1 Qualitative m.o. scheme for (*a*) $[MMe(\eta\text{-}C_5H_5)(CO)_3]$, (*b*) $[MMe(\eta\text{-}C_5H_5)(CO)_2]$, and (*c*) $[Fe(CH_2CN)(\eta\text{-}C_5H_5)(CO)_2]$

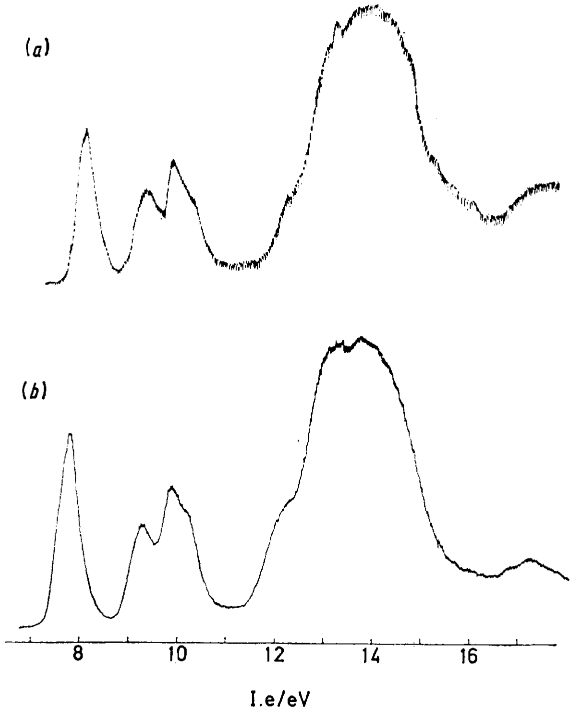

FIGURE 2 P.e. spectrum of $[MMe(\eta\text{-}C_5H_5)(CO)_3]$ [M = Mo (*a*) and W (*b*)]

Above 9.5 eV the spectra resemble that of $[Mn(\eta\text{-}C_5H_5)(CO)_3]$, although a shoulder appeared at 12.2 (Mo) and 12.3 eV (W) which is absent from the $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ spectrum. This band may be assigned to ionization from the C–H bonding orbitals of the methyl group. The bands at 9.7 and 10.0. eV (Mo) and 9.9 and 10.2 eV (W) are similar in shape and ionization energy (i.e.) to the bands assigned to C_5H_5 e ionizations in $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ and so are assigned to the corresponding $4a' + 2a''$ ionizations of $[MMe(\eta\text{-}C_5H_5)(CO)_3]$. The only remaining band which has no counterpart in the $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ spectrum is that at 9.07 (Mo) and 9.26 eV (W) which is therefore assigned to the $5a'$ orbital, corresponding to the metal–carbon σ bond.

$[MMe(\eta\text{-}C_5H_5)(CO)_2]$ (M = Fe *or* Ru).—Bonding in the $M(CO)_2$ group has been discussed by Kettle[12] and Orgel,[13] although Orgel neglects π bonding to the CO ligands. The $M(CO)_2$ unit is of local symmetry C_{2v} and it can be shown that if the group lies in the yz plane the carbonyl σ orbitals transform as $a_1 + b_2$, the radial π orbitals as $a_1 + b_2$, and the tangential π orbitals as $a_2 + b_1$. Combination of the two CO ligands with a $M(\eta\text{-}C_5H_5)$ group lifts the degeneracy of the e_1 and e_2 orbitals of this group transforming them to $b_1 + b_2$ and $a_1 + a_2$ respectively.

Figure 1(*b*) shows the interaction of the metal–carbon σ-bonding orbital with the $M(\eta\text{-}C_5H_5)(CO)_2$ orbitals in C_s symmetry to form a m.o. scheme for $[MMe(\eta\text{-}C_5H_5)(CO)_2]$. There are now six electrons occupying orbitals which are mainly metal in character. In this respect the $Me(CO)_2$ ligand group resembles a cyclopentadienyl ligand and the $[MMe(\eta\text{-}C_5H_5)(CO)_2]$ molecules may be compared with the corresponding $[M(\eta\text{-}C_5H_5)_2]$. The

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[12] S. F. A. Kettle, *J. Chem. Soc. (A)*, 1966, 420.

[13] L. E. Orgel, *J. Inorg. Nuclear Chem.*, 1956, **2**, 315.

spectra of [MMe(η-C_5H_5)$(CO)_2$] (M = Fe and Ru) (see Figure 3) are less alike than those of [MMe(η-C_5H_5)$(CO)_3$] (M = Mo and W), reflecting the larger difference between first- and second-row metals, also seen in the Group 8 [M(η-C_5H_5)$_2$].[14] The assignments (Table 2) will therefore be made separately.

Ionizations above 11 eV showed an amorphous band similar to those found in all the other cyclopentadienyl spectra except that the [FeMe(η-C_5H_5)$(CO)_2$] spectrum had a shoulder at 12.1 eV, similar to the ones found for [MMe(η-C_5H_5)$(CO)_3$] (M = Mo and W) assigned to Me ionizations. The band at 9.90 eV with a slight shoulder to high i.e. is similar to the bands assigned to C_5H_5 e_1 ionizations in other carbonylcyclopentadienylmetal spectra, and is therefore assigned to the $3a' + 2a''$ ionizations. The three remaining bands must correspond to the four remaining occupied orbitals of Figure 1. For intensity reasons, the band at 7.78 eV must be due to ionizations from both the $6a'$ and the $3a''$ orbitals. The band at 8.53 eV then corresponds to the $5a'$ ionizations and the band at 9.15 eV to the $4a'$ ionizations corresponding to the metal–carbon σ bond. It is interesting to note that the bands at 7.78 and 8.53 eV resemble the e_{2g} and a_{1g} bands of ferrocene, but shifted by 1—1.3 eV to higher i.e.

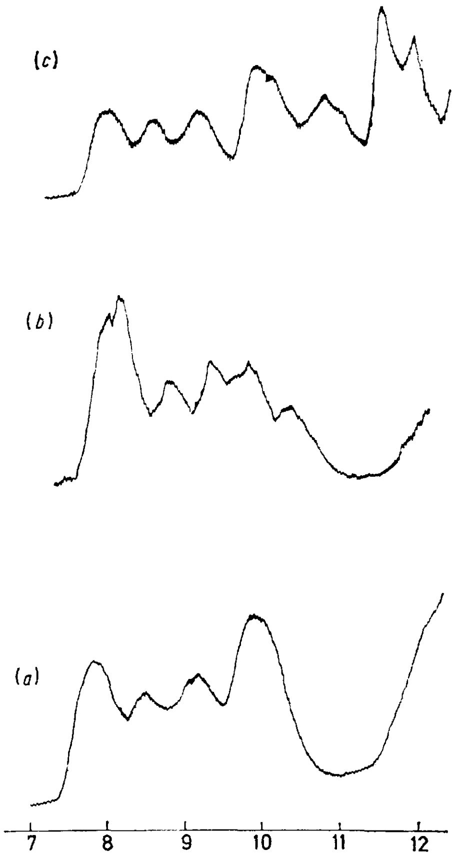

FIGURE 3 P.e. spectra of (a) [FeMe(η-C_5H_5)$(CO)_3$], [RuMe(η-C_5H_5)$(CO)_2$], and (c) [Fe(CH_2CN)(η-C_5H_5)$(CO)_2$]

Whereas the spectrum of [FeMe(η-C_5H_5)$(CO)_2$] has four bands below 11 eV, that of [RuMe(η-C_5H_5)$(CO)_2$] has five, and in addition the lowest i.e. band has a shoulder to low i.e.; the second-row element shows greater splitting as is found in the spectra of [M(η-C_5H_5)$_2$].[14] The spectrum is assigned by comparison with that of the iron analogue. The bands at 8.29 and 8.96 eV are assigned to the $6a' + 3a''$ and the $5a'$ orbitals respectively, the splitting of the band at 8.29 eV indicating the emergence of the $6a'$ ionizations to low i.e. The band at 9.48 eV is assigned to the $4a'$ ionizations and the bands at 9.98 and 10.51 eV to the $2a'' + 3a'$ ionizations respectively.

[Fe(CH_2CN)(η-C_5H_5)$(CO)_2$].—Methyl cyanide, in addition to a broad band at 15—19 eV corresponding to methyl ionizations, has two very sharp bands at 13.14 and 12.21 eV which have been assigned to the nitrogen lone-pair σ orbital and to the highest C≡N π orbital respectively.[15] The two sharp peaks at 12.27 and 11.89 eV in the spectrum of [Fe(CH_2CN)(η-C_5H_5)$(CO)_2$] [see Figure 3(*c*)] are similarly assigned to ionizations from the CN group, showing a lowering in i.e. of 0.87 and 0.32 eV respectively. The most intense of the remaining bands, at 10.25 eV, has the same band contour as bands assigned to ionizations from the C_5H_5 e_1 m.o. in the other molecules of this series, and is assigned to ionizations from the $6a' + 2a''$ orbitals [see Figure 1(*c*)]. The i.e. of this band is higher than found for other C_5H_5 e_1 ionizations, and this is explained by the electron-withdrawing nature of the CN group.

There are now four remaining bands of approximately equal intensity to assign, corresponding to six metal electrons and the electron pair of the Fe–C bond. It seems reasonable to assign the bands at 8.29, 8.90, and 9.48 eV to ionizations from the three mainly metal orbitals $8a'$, $3a''$, and $7a'$, and the band at 11.14 eV to ionization from the metal–carbon bonding $5a'$ orbital. Under this assignment, the intense band at 7.78 eV in [FeMe(η-C_5H_5)$(CO)_2$] has split into two separate bands in [Fe(CH_2CN)(η-C_5H_5)$(CO)_2$], which is reasonable from the intensity variations.

The average *d*-orbital i.e. has increased by 0.87 eV, while the metal–carbon σ i.e. has increased by 2.1 eV from the corresponding values in [FeMe(η-C_5H_5)$(CO)_2$]. At first sight this shift of over 2 eV seems particularly large compared with the other band shifts for [Fe(CH_2CN)(η-C_5H_5)$(CO)_2$]. However, the carbon which bonds to the metal is the same atom on which substitution of H for C≡N occurs. The M–C σ bond may then undergo the same sort of change as the C–H bonds in methane when one of the hydrogens is replaced by CN. Comparison of the CH_4 and MeCN spectra reveals that here a shift of *ca.* 2 eV occurs.[15]

Symon and Waddington[5] also reported the p.e.

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[14] S. Evans, M. L. H. Green, B. Jewitt, A. F. Orchard, and C. F. Pygall, *J.C.S. Faraday II*, 1972, 1847.

[15] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy,' Wiley–Interscience, 1970.

spectrum of [FeMe(η-C_5H_5)$(CO)_2$].[†] Their tabulated i.e.s are in reasonable agreement with our values given the broad nature of the ionization bands. They distinguish two ionizations present in the first band but we were unable to do so. Since their spectrum is not displayed further comparison is not possible. They assign the metal–carbon σ i.e. for [FeMe(η-C_5H_5)$(CO)_2$] to the band at 8.68 eV (our value 8.53 eV). Supporting evidence cited is the assignment by Lichtenberger and Fenske[17] of the Mn–C σ ionization in [MnMe$(CO)_5$] to a band at 8.65 eV. Work by Higginson *et al.*[4] suggests that a more likely assignment is to the band at 9.49 eV, in the [MnMe$(CO)_5$] spectrum. We prefer our assignment of the Fe–C ionization to the band at 9.15 eV, in reasonable agreement with the assignment for [MMe(η-C_5H_5)$(CO)_3$] given above and those for [MMe$(CO)_5$] (M = Mn and Re).

In Table 3 we list some compounds containing transition-metal–carbon σ bonds whose i.e.s have been assigned. It can be seen that the higher i.e.s (or higher average i.e.s) arise from compounds of metals to the right of the transition series and from those with a substantial number of carbonyl groups.

TABLE 3

Ionization energies (eV) of M–C bonds

Compound	I.e.			Weighted average
WMe_6[2]	8.61	9.33	10.17	9.11
$ReMe_6$ *	8.47	9.77	10.48	9.24
$Cr(CH_2CMe_3)_4$[1]	8.37			
$Cr(CH_2SiMe_3)_4$[1]	8.69			
[MnMe$(CO)_5$][4]	9.49			
[ReMe$(CO)_5$][4]	9.51			
[$MoMe_2$(η-C_5H_5)$_2$][3]	8.3, 9.6			8.95
[WMe_2(η-C_5H_5)$_2$][3]	8.3, 9.6			8.95
[MoMe(η-C_5H_5)$(CO)_3$]	9.07			
[WMe(η-C_5H_5)$(CO)_3$]	9.26			
[FeMe(η-C_5H_5)$(CO)_2$]	9.15			
[RuMe(η-C_5H_5)$(CO)_2$]	9.48			

* J. C. Green, unpublished work.

We thank the S.R.C. for a studentship (to S. E. J.) and for a grant to purchase the spectrometer, and Dr. M. G. Swanick for a sample of [RuMe(η-C_5H_5)$(CO)_2$].

[6/310 *Received*, 13*th February*, 1976]

[†] The various assignments of these workers are based on the assignments of the p.e. spectrum of [Fe(η-C_5H_5)$_2$]. Unfortunately, in the introduction to their paper they give an assignment of ferrocene differing substantially from that given in the reference they quote. The normal assignment[14] is 6.90 (e_{2g}) 7.20 (a_{1g}), 8.75 and 9.40 (e_{1u} and e_{1g}), and 12.25 eV and subsequent bands (a_{2u} and σ structure of ring). Symon and Waddington imply 6.90 and 7.20 (a_{1g}), 8.75 and 9.40 (e_{2g}), and 12—14 eV (e_{1g}, e_{1u}, and a_{2u}). The spectrum of [{Fe(η-C_5H_5)(CO)}$_4$] shown by these authors[5] is very similar to that of ferrocene but differs in i.e. by 0.3 eV. It also shows evidence of free carbon monoxide which has a sharp ionization at 14 eV and a vibrational sequence between 16.5 and 17.5 eV. This compound is known to decompose thermally to ferrocene.[16]

[16] R. B. King, *Inorg. Chem.*, 1966, **5**, 2227.

[17] D. L. Lichtenberger and R. F. Fenske, *Inorg. Chem.*, 1974, **13**, 486.