(24) Calculated from data of L. I. B. Haines and A. J. Poë, *J. Chem. Soc. A*, 2826 (1969).
(25) L. S. Benner and A. L. Balch, *J. Organomet. Chem.*, **134**, 121 (1977).
(26) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967, p 572.
(27) (a) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970); (b) C. A. Tolman, W. C. Seidel, and L. Gosser, *ibid.*, **96**, 53 (1974).
(28) L. E. Manzer and C. A. Tolman, *J. Am. Chem. Soc.*, **97**, 1955 (1975).
(29) R. A. Levenson, H. B. Gray, and G. P. Ceasar, *J. Am. Chem. Soc.*, **92**, 3653 (1970).
(30) R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc.*, **97**, 6042 (1975).
(31) P. Lemoine and M. Gross, *J. Organomet. Chem.*, **133**, 193 (1977).
(32) A fuller discussion of these and other related data will be given elsewhere.
(33) M. J. Bennett and R. Mason, *J. Chem. Soc. A*, 75 (1968); M. Laing, T. Ashworth, P. Sommerville, E. Singleton, and R. Reiman, *J. Chem. Soc., Chem. Commun.*, 1251 (1972); M. Laing, E. Singleton, and R. Reiman, *J. Organomet. Chem.*, **56**, C21 (1973).
(34) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1140 (1965).
(35) M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967); N. N. Nesmeyanov, K. M. Anisimov, N. E. Kolobova, and I. S. Kolomnikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 194 (1963); *Chem. Abstr.*, **58**, 9870*c* (1963).
(36) J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J. Chem. Soc., Chem. Commun.*, 267 (1973).
(37) A plot made by using values of $h\nu(\sigma \rightarrow \sigma^*)$ from low-temperature spectra is somewhat better, with data for $M_2(CO)_{10}$ ($M_2$ = $Mn_2$, MnRe, and $Re_2$) lying exactly on a straight line and those for $Tc_2(CO)_{10}$ being slightly below it. However, since values of $h\nu(\sigma \rightarrow \sigma^*)$ for almost all the substituted complexes are available only from room-temperature spectra, we shall continue to use them.

---

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

# Preparation and Photochemistry of Metal–Metal Bonded Heterodinuclear Precursors to Tetracarbonylcobalt(0), Tricarbonyl($\eta^5$-cyclopentadienyl)molybdenum(I), Tricarbonyl($\eta^5$-cyclopentadienyl)tungsten(I), and Dicarbonyl($\eta^5$-cyclopentadienyl)iron(I)

HARMON B. ABRAHAMSON and MARK S. WRIGHTON*[1]

*Received September 14, 1977*

Photochemistry and electronic spectra of $(\eta^5\text{-}C_5H_5)(CO)_3MCo(CO)_4$ and $(\eta^5\text{-}C_5H_5)(CO)_3MFe(CO)_2(\eta^5\text{-}C_5H_5)$ (M = Mo, W) are reported. These heterodinuclear (M–M′) species have been prepared by photolysis of mixtures of the appropriate homodinuclear metal carbonyls M–M and M′–M′. These M–M′ species exhibit low-energy absorptions which are attributable to $d\pi \rightarrow \sigma^*$ (absorption maximum 510–545 nm, $\epsilon$ in the range 460–1340 L mol$^{-1}$ cm$^{-1}$) and $\sigma_b \rightarrow \sigma^*$ (absorption maximum 340–398 nm, $\epsilon$ in the range 10 000–14 000 L mol$^{-1}$ cm$^{-1}$) transitions. The spectral data allow a prediction of the position of the $\sigma_b \rightarrow \sigma^*$ absorption as ~415 nm in the nonbridged form of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. Photoexcitation of the M–M′ complexes results in chemistry implicating homolytic cleavage of the metal–metal bond. In degassed benzene solutions, flash photolysis of M–M′ results in the formation of a 1:1 ratio of products M–M and M′–M′. Based on the disappearance of M–M′, the yield of M–M and M′–M′ is >90%. Irradiation of M–M′ in degassed $CCl_4$ solution at 366 nm gives essentially stoichiometric amounts of $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, but the fate of $Co(CO)_4$ was found to be mainly coupling to form $Co_2(CO)_8$. The M–M′ disappearance quantum yield in $CCl_4$ at 366 nm is in the range 0.3–0.5. Irradiation of M–M′ in benzene solutions of 0.1 M 1-$IC_5H_{11}$ or $CCl_4$ results in a mixture of M–M, M′–M′, and metal carbonyl halides. Such data establish the ordering of metal radical reactivity toward halogen atom abstraction as $(\eta^5\text{-}C_5H_5)W(CO)_3$ > $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ > $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ > $Co(CO)_4$.

Photochemical studies of dinuclear metal carbonyls containing a direct metal–metal bond have shown that population of the lowest excited states results in efficient homolytic cleavage of the metal–metal bond, reaction 1.[2-11] The re-

$$M\text{–}M \xrightarrow{h\nu} M\cdot + \cdot M \tag{1}$$

sulting 17e$^-$ species (1) can be trapped with spin-traps,[3,4] (2) react with halocarbons to give net abstraction products,[2,5,6] (3) couple at essentially diffusion-controlled rates,[7,8] (4) are substitution labile,[2,9] and (5) apparently disproportionate under certain conditions resulting in the formation of metal carbonyl anions.[10,11] In a preliminary account[12] we reported on the photochemistry of some heterodinuclear metal–metal bonded compounds in connection with ordering the reactivity of the 17e$^-$ fragments. In this paper we report the synthesis, characterization, and photochemistry of $(\eta^5\text{-}C_5H_5)(CO)_3MCo(CO)_4$ and $(\eta^5\text{-}C_5H_5)(CO)_3MFe(CO)_2(\eta^5\text{-}C_5H_5)$ (M = Mo, W). According to the d$^n$ configuration at the central metal, these molecules can be categorized as "d$^5$–d$^9$" and "d$^5$–d$^7$" dimers. Thus, these molecules are precursors to 17e$^-$ fragments of d$^5$, d$^7$, or d$^9$ configurations.

## Results and Discussion

**Preparation of the Complexes.** The M–M′ bonded complexes have been prepared by the near-UV irradiation of the appropriate M–M and M′–M′ complexes in hydrocarbon solvents, reactions 2 and 3. The details are given in the

$$Co_2(CO)_8 + (\eta^5\text{-}C_5H_5)_2M_2(CO)_6 \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)(CO)_3MCo(CO)_4 \tag{2}$$

M = Mo, W

$$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4 + (\eta^5\text{-}C_5H_5)_2M_2(CO)_6 \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)(CO)_3MFe(CO)_2(\eta^5\text{-}C_5H_5) \tag{3}$$

M = Mo, W

Experimental Section but it is noteworthy that the photochemical procedure gives respectable yields of the products based on the $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ disappearance. The photosensitivity of the products precludes truly high product yields, but the procedure does allow the synthesis of useful quantities of the M–M′ species.

**Spectral Properties of the Complexes.** The electronic spectra of the four complexes in EPA solution at 298 and 77 K are given in Figure 1, and band maxima and absorptivities are listed in Table I. By analogy to other dinuclear metal–metal bonded complexes,[2,5,13] we assign the near-UV absorption to a $\sigma_b \rightarrow \sigma^*$ transition, and the visible band is attributable to a $\pi d \rightarrow \sigma^*$ transition. We note that the $\sigma_b \rightarrow \sigma^*$ absorption is at higher energy for the W compared to the analogous Mo complex. Further, it has been noted that the $\sigma_b \rightarrow \sigma^*$ position of M–M′ complexes is often situated between that for the M–M and M′–M′ complexes. A major conclusion drawn from such considerations is that the M–M′ bonding in the heterodinuclear metal carbonyls has relatively little ionic character. Thus, the $\sigma_b \rightarrow \sigma^*$ absorptions for $Co_2(CO)_8$ (nonbridged) and

0020-1669/78/1317-1003$01.00/0

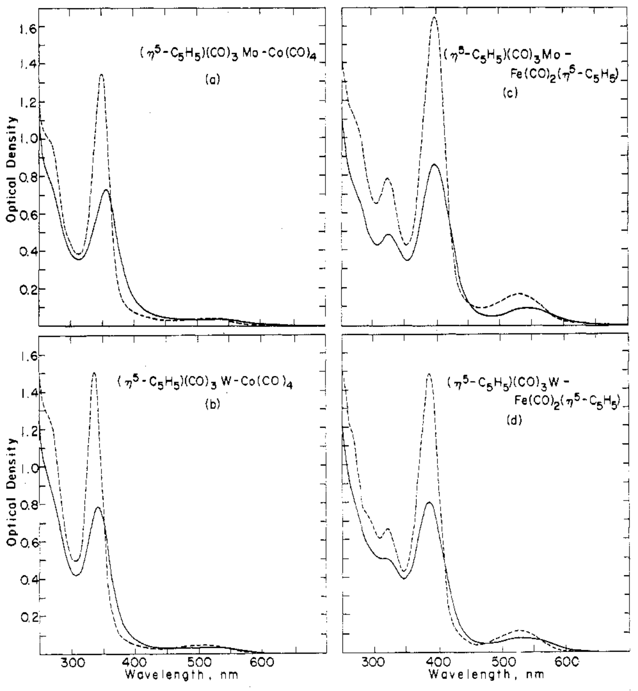

**Figure 1.** Optical absorption spectra of complexes at 298 K (—) and 77 K (---) in EPA solution. Spectral changes upon cooling from 298 to 77 K are not corrected for solvent contraction; cf. Table I for spectral maxima and molar absorptivities.

**Table I.** Electronic Absorption Spectral Data for M–M′ at 298 K

| Complex | Solvent | Bands, nm ($\epsilon$)[a] |
|---|---|---|
| $(\eta^5\text{-}C_5H_5)(CO)_3MoCo(CO)_4$ | $C_6H_6$ | 524 (510), 357 (14 300) |
| | $CCl_4$ | 526 (460), 357 (11 600) |
| | EPA | 520 (*0.04*), 354 (*0.73*) |
| $(\eta^5\text{-}C_5H_5)(CO)_3WCo(CO)_4$ | $C_6H_6$ | 510 (560), 343 (12 300) |
| | $CCl_4$ | 513 (500), 342 (10 700) |
| | EPA | 514 (*0.03*), 340 (*0.79*) |
| $(\eta^5\text{-}C_5H_5)(CO)_3MoFe(CO)_2\text{-}(\eta^5\text{-}C_5H_5)$ | $C_6H_6$ | 543 (1340), 398 (12 300), 327 (6500) |
| | $CCl_4$ | 545 (1230), 398 (11 800), 326 (6460) |
| | EPA | 542 (*0.09*), 396 (*0.86*), 323 (*0.48*) |
| $(\eta^5\text{-}C_5H_5)(CO)_3WFe(CO)_2\text{-}(\eta^5\text{-}C_5H_5)$ | $C_6H_6$ | 534 (1150), 388 (12 100), 320 (6350) |
| | $CCl_4$ | 535 (1110), 388 (12 400), 320 sh |
| | EPA | 535 (*0.08*), 386 (*0.80*), 320 (*0.50*) |

[a] Italic values in parentheses are relative absorptivities.

$(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ bracket that for $(\eta^5\text{-}C_5H_5)(CO)_3MCo(CO)_4$. If such a relationship is true for the $(\eta^5\text{-}C_5H_5)(CO)_3MFe(CO)_2(\eta^5\text{-}C_5H_5)$, we can predict the position of the $\sigma_b \rightarrow \sigma^*$ transition for a nonbridged $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ to be at about 415 nm. This number is based on the known band positions of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$[5] and those reported here for $(\eta^5\text{-}C_5H_5)(CO)_3MFe(CO)_2(\eta^5\text{-}C_5H_5)$ according to the procedure previously suggested.[14] Quite interestingly, we predicted ~430 nm for the $\sigma_b \rightarrow \sigma^*$ position in nonbridged $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ from the $\sigma_b \rightarrow \sigma^*$ positions in $M_2(CO)_{10}$[2] and $(\eta^5\text{-}C_5H_5)(CO)_2FeM(CO)_5$ (M = Mn, Re).[15] The agreement between the two predicted values is satisfactory. Since $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ is principally bridged in solution, the $\sigma_b \rightarrow \sigma^*$ absorption in the nonbridged form has not been observed. The $\sigma_b \rightarrow \sigma^*$ absorption for the bridged compound has been tentatively associated with a band at ~340 nm.[16]

**Table II.** Infrared Spectral Data for M–M′ and Products at 298 K

| Complex | Solvent | Bands, cm$^{-1}$ ($\epsilon$) |
|---|---|---|
| $(\eta^5\text{-}C_5H_5)(CO)_3\text{-}MoCo(CO)_4$ | $C_6H_6$ | 2072 (2800), 2016 (4250), 1987 sh, 1972 (4750), 1940 sh, 1929 (1930) |
| | $CCl_4$ | 2076 (3680), 2021 (5190), 1984 sh, 1976 (4830), 1946 (1950), 1938 (1830) |
| $(\eta^5\text{-}C_5H_5)(CO)_3\text{-}WCo(CO)_4$ | $C_6H_6$ | 2074 (2460), 2016 (3260), 1982 (3340), 1972 (3720), 1927 sh, 1918 (2180) |
| | $CCl_4$ | 2077 (3790), 2021 (5160), 1986 (3940), 1975 (4680), 1945 (2150), 1936 (2310) |
| $(\eta^5\text{-}C_5H_5)(CO)_3\text{-}MoFe(CO)_2\text{-}(\eta^5\text{-}C_5H_5)$ | $C_6H_6$ | 2010 (140), 1996 (200), 1950 (5720), 1937 (4920), 1889 sh, 1877 (2110) |
| | $CCl_4$ | 2015 (150), 1999 (250), 1956 (6310), 1942 (4560), 1887 (1290), 1885 (1950) |
| $(\eta^5\text{-}C_5H_5)(CO)_3\text{-}WFe(CO)_2(\eta^5\text{-}C_5H_5)$ | $C_6H_6$ | 2010 (150), 1994 (290), 1948 (6700), 1936 (5150), 1884 sh, 1872 (3280) |
| | $CCl_4$ | 2016 (90), 1998 (340), 1954 (8420), 1940 (5490), 1891 (1690), 1878 (2620) |
| $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ | $C_6H_6$ | 2014 (490), 1955 (8420), 1910 (6540) |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ | $C_6H_6$ | 2053 (2150), 1977 (3340), 1961 (1590) |
| | $CCl_4$ | 2058 (2800), 1986 (3830), 1963 (1840) |
| $(\eta^5\text{-}C_5H_5)Mo(CO)_3I$ | $C_6H_6$ | 2039 (3070), 1965 (3620) |
| $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ | $C_6H_6$ | 2010 (310), 1951 (9430), 1902 (7000), 1893 sh |
| $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ | $C_6H_6$ | 2045 (2490), 1958 (3680), 1946 sh |
| | $CCl_4$ | 2051 (3330), 1969 (5050), 1949 (2390) |
| $(\eta^5\text{-}C_5H_5)W(CO)_3I$ | $C_6H_6$ | 2033 (3160), 1952 (4000) |
| $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ | $C_6H_6$ | 1996 (2770), 1952 (2440), 1781 (4130) |
| $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ | $C_6H_6$ | 2049 (2270), 2003 (2340) |
| | $CCl_4$ | 2055 (3060), 2012 (3020), 1980 (80) |
| $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ | $C_6H_6$ | 2037 (2370), 1993 (2490) |
| $Co_2(CO)_8$ | $C_6H_6$ | 2071 (3780), 2041 (3420), 2022 (2940), 1896 (970) |
| $Co_3(CO)_9CCl$ | $C_6H_6$ | 2109 (910), 2061 (14 900), 2044 (7000), 2030 (1640) |
| | $CCl_4$ | 2109 (1060), 2062 (25 900), 2045 (11 700), 2030 (1400), 1986 (120) |

For $Co_2(CO)_8$ it was found that the $\sigma_b \rightarrow \sigma^*$ absorption is ~7000 cm$^{-1}$ higher in energy in the bridged compared to the nonbridged form. Likewise, spectral data[17] for the $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$ show that the bridged isomer has a $\sigma_b \rightarrow \sigma^*$ absorption ~7000 cm$^{-1}$ above that for the nonbridged form. Assuming a similar relationship for the two $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ species, the predicted 415–430-nm position for the nonbridged form seems reasonable.

Analysis of the photoreactions of the M–M′ species was carried out by infrared spectroscopy. Infrared band maxima and absorptivities for starting materials and authentic samples of photoproducts are given in Table II. From the infrared spectra in solution there is no evidence for bridging CO in any of the four M–M′ complexes studied.

**Flash-Photolysis Studies in Benzene Solution.** Benzene solutions of the M–M′ complexes were flash photolyzed and the resulting products were identified as the M–M and M′–M′ species. The infrared spectral changes resulting from the flash photolysis of $(\eta^5\text{-}C_5H_5)(CO)_3WCo(CO)_4$, Figure 2, are representative, and Table III shows quantitative data for each of the complexes. The general result is that M–M and M′–M′

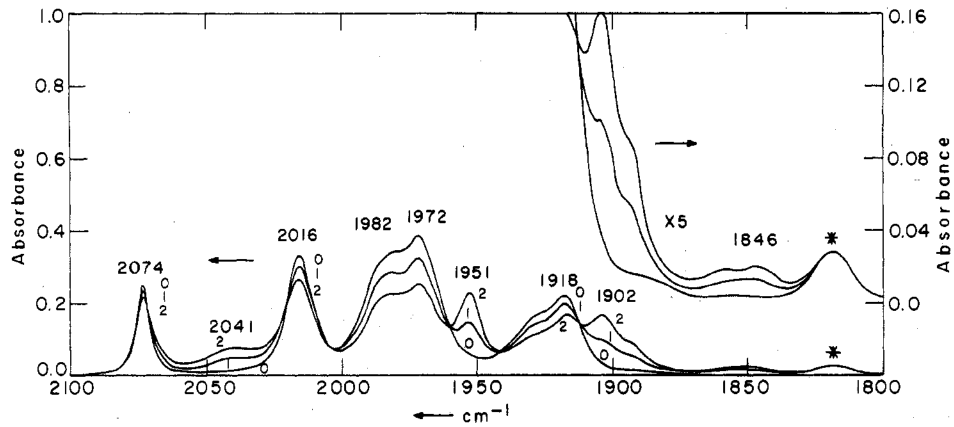

**Figure 2.** Infrared spectral changes subsequent to the flash photolysis of 0.01 M $(\eta^5\text{-}C_5H_5)(CO)_3WCo(CO)_4$ in benzene solution. The band denoted by * is due to solvent absorption; bands at 2074, 2016, 1982, 1972, and 1918 cm$^{-1}$ are due to starting complex. Bands at 2041 and 1846 cm$^{-1}$ are characteristic of $Co_2(CO)_8$ and those at 1951 and 1902 cm$^{-1}$ are due to $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$. Curves 0, 1, and 2 are at zero time, after one flash, and after three flashes, respectively; cf. Table III for quantitative results.

**Table III.** Flash-Photolysis Experiments with M–M′[a]

| Starting complexes (mol × $10^6$) | No. of flashes | Mol reacted × $10^6$ | Products (mol formed × $10^6$) |
|---|---|---|---|
| $(\eta^5\text{-}C_5H_5)(CO)_3\text{-}MoCo(CO)_4$ (12.9) | 2 | 3.29 | $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (1.83)<br>$Co_2(CO)_8$ (1.86) |
|  | 3 | 4.25 | $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (2.18)<br>$Co_2(CO)_8$ (2.30) |
| $(\eta^5\text{-}C_5H_5)(CO)_3\text{-}WCo(CO)_4$ (10.2) | 1 | 1.92 | $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ (1.04)<br>$Co_2(CO)_8$ (0.97) |
|  | 3 | 3.65 | $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ (1.93)<br>$Co_2(CO)_8$ (1.83) |
| $(\eta^5\text{-}C_5H_5)(CO)_3\text{-}MoFe(CO)_2(\eta^5\text{-}C_5H_5)$ (14.0) | 2 | 2.72 | $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (1.19)<br>$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (1.41) |
| $(\eta^5\text{-}C_5H_5)(CO)_3\text{-}WFe(CO)_2(\eta^5\text{-}C_5H_5)^b$ (3.2) | 2 | 0.33 | $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ (0.17)<br>$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (0.16) |
|  | 3 | 0.42 | $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ (0.20)<br>$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (0.20) |

[a] Flash photolysis of 1 mL of degassed benzene solutions of the M-M′ complex in Pyrex ampules. Flashes were at 2000 J and analyses were carried out by IR spectral changes. [b] Flashes at 500 J.

are formed in a 1:1 ratio and the yield of these products is >90% based on the disappearance of M–M′. The flash-photolysis procedure was chosen in order to generate high concentrations of the intermediates which must couple in a bimolecular reaction to give the resulting metal–metal bonded species. Low-intensity, continuous irradiation does give the cross-coupled products (vide infra), but the flash procedure is a convenient way to minimize the effect of solvent impurities which may scavenge the intermediates. The data in Table III provide substantial evidence for photoinduced, homolytic scission of the M–M′ bond in the species studied here.

**Irradiation in the Presence of Halocarbons.** Irradiation of the M–M′ species in neat $CCl_4$ leads to efficient disappearance of the M–M′-bonded species. Disappearance quantum yields upon 366-nm irradiation are given in Table IV. For $(\eta^5\text{-}C_5H_5)(CO)_3MFe(CO)_2(\eta^5\text{-}C_5H_5)$ the chemistry proceeds according to reaction 4, with respect to the organometallic

$$(\eta^5\text{-}C_5H_5)(CO)_3MFe(CO)_2(\eta^5\text{-}C_5H_5) \xrightarrow[CCl_4]{h\nu} (\eta^5\text{-}C_5H_5)M(CO)_3Cl + (\eta^5\text{-}C_5H_5)Fe(CO)_2Cl \qquad (4)$$

M = Mo, W

products. For the $(\eta^5\text{-}C_5H_5)(CO)_3MCo(CO)_4$ complexes the only well-characterized product is $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ (M = Mo, W). The fate of the $Co(CO)_4$ fragment is not known; in some cases we have observed trace quantities of $Co_3(CO)_9CCl$ which also is found in the thermal or photochemical reaction of $Co_2(CO)_8$ in pure $CCl_4$. There is the possibility that $Co(CO)_4Cl$ is formed but subsequently thermally decomposes.

**Table IV.** Quantum Yields for M–M′ in $CCl_4$ at 366 nm[a]

| Complex M–M′ | $\Phi_{disapp}$ M–M′ | $\Phi_{app}$ M–Cl | $\Phi_{app}$ M′–Cl |
|---|---|---|---|
| $(\eta^5\text{-}C_5H_5)(CO)_3MoCo(CO)_4$ | 0.50 | 0.60 | *b* |
| $(\eta^5\text{-}C_5H_5)(CO)_3WCo(CO)_4$ | 0.37 | 0.34 | *b* |
| $(\eta^5\text{-}C_5H_5)(CO)_3MoFe(CO)_2(\eta^5\text{-}C_5H_5)$ | 0.30 | 0.30 | 0.35 |
| $(\eta^5\text{-}C_5H_5)(CO)_3WFe(CO)_2(\eta^5\text{-}C_5H_5)$ | 0.47 | 0.36 | 0.41 |

[a] Photolysis in degassed $CCl_4$ solution at 25 °C. Analysis by IR spectral changes. The products of the photolysis are $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$. [b] No cobalt carbonyl chloride products observed. See text.

Irradiation of the M–M′ complexes in benzene solutions containing 0.1 M $CCl_4$ or $1\text{-}IC_5H_{11}$ generally gives a mixture of metal carbonyl halide and M–M products, Table V. Representative infrared spectral changes accompanying the reaction are given in Figure 3. At such low concentrations of halocarbon we found that the $Co(CO)_4$ fragments form mainly $Co_2(CO)_8$. Indeed, in the presence of 0.1 M $1\text{-}IC_5H_{11}$ the yield of $Co_2(CO)_8$ is essentially quantitative. The implication is that the $Co(CO)_4$ is virtually unreactive toward $1\text{-}IC_5H_{11}$ and couples at a rate which is faster than reactions leading to decomposition via halogen abstraction. Incidentally, irradiation of $Co_2(CO)_8$ in the presence of $1\text{-}IC_5H_{11}$ does not lead to significant consumption of the halocarbon. This confirms that the $Co(CO)_4$ fragments do not abstract halogen from $1\text{-}IC_5H_{11}$ to give product(s) which result in subsequent regeneration of $Co_2(CO)_8$ and dehalogenation of the alkyl halide. Degassed ampules of alkane solutions of 0.01 M $Co_2(CO)_8$ and 0.1 M $1\text{-}IC_5H_{11}$ yield $Co_4(CO)_{12}$ upon prolonged irradiation. In 0.1 M $CCl_4$ there is definitely evidence for $Co(CO)_4$ reaction, perhaps to give the unstable $Co(CO)_4Cl$; but again only small amounts of the $Co_3(CO)_9CCl$ are found, while the major product is still $Co_2(CO)_8$. Flash photolysis of the $(\eta^5\text{-}C_5H_5)(CO)_3WCo(CO)_4$ was carried out in the presence of 0.1 M $CCl_4$. The higher metal radical concentration produced by the flash results in a larger fraction of M–M coupling products. Such is expected, since metal radical coupling is bimolecular in metal radicals while halogen abstraction is first order in metal radicals. Under the flash

**Table V.** Photolysis of M-M' in Benzene Solutions of RX[a]

| | | | Mol of products × $10^8$ [d] | | | | |
|---|---|---|---|---|---|---|---|
| M-M' (concn, mM)[b] | RX[c] | Mol of M-M' consumed × $10^8$ | M-M | M-X | M'-M' | M'-X | Irrad time, s |
| Mo-Co (25) | 1-$IC_5H_{11}$ | 8.86 | 4.56 | 0.44 | 4.36 | *e* | 60 |
| W-Co (35) | 1-$IC_5H_{11}$ | 3.76 | 0.98 | 2.56 | 1.78 | *e* | 10 |
| Mo-Fe (9) | 1-$IC_5H_{11}$ | 3.46 | 1.06 | 1.34 | 1.50 | 0.46 | 60 |
| W-Fe (6) | 1-$IC_5H_{11}$ | 1.74 | *e* | 1.78 | 0.94 | *e* | 35 |
| Mo-Co (13) | $CCl_4$ | 3.52 | 0.28 | 2.98 | 1.28 | *f, g* | 10 |
| W-Co (41) | $CCl_4$ | 5.96 | *e* | 5.76 | 1.24 | 0.35[f] | 10 |
| W-Co (10) | $CCl_4$ | 1.06 | 0.41 | 0.24 | 0.51 | *e* | *h* |
| Mo-Fe (11) | $CCl_4$ | 3.80 | *e* | 3.72 | *e* | 3.42 | 15 |
| W-Fe (8) | $CCl_4$ | 3.70 | *e* | 3.80 | *e* | 3.62 | 30 |

[a] M-M' complexes irradiated in deoxygenated benzene solutions of RX at 25 °C using a GE Black Light source equipped with two 15-W bulbs with output between 300 and 400 nm. [b] M-M' complexes: Co is $Co(CO)_4$, Mo is $Mo(CO)_3(\eta^5\text{-}C_5H_5)$, W is $W(CO)_3(\eta^5\text{-}C_5H_5)$, Fe is $Fe(CO)_2(\eta^5\text{-}C_5H_5)$. [c] RX concentration was 0.10 M. [d] Products from irradiation IR analyzed by comparison with authentic samples. M-X is metal carbonyl halide, $M_2$ is homodinuclear complex. Results are based on an irradiated volume of $2 \times 10^{-2}$ mL. [e] No product detectable. [f] Product is $(CO)_9Co_3CCl$. [g] Trace present, not measurable. [h] Solution was flash photolyzed using a Xenon Corp. flash apparatus.

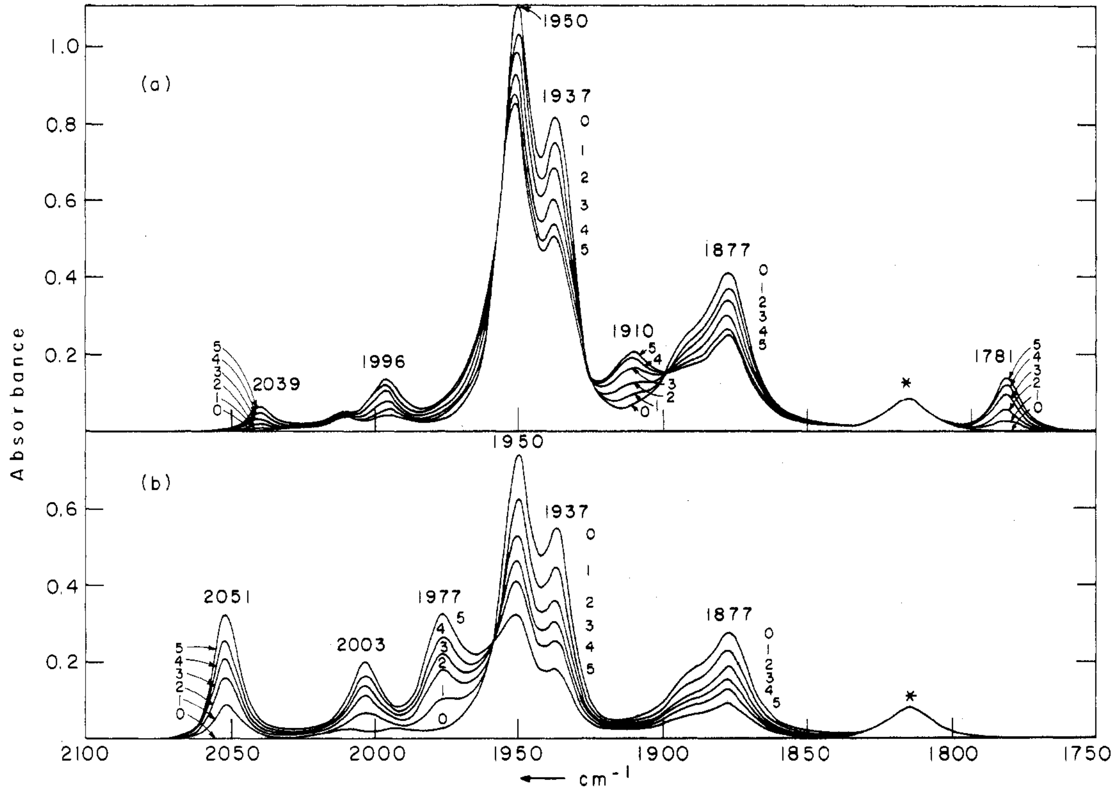

**Figure 3.** Infrared spectral changes accompanying irradiation of $(\eta^5\text{-}C_5H_5)(CO)_3MoFe(CO)_2(\eta^5\text{-}C_5H_5)$ in benzene solutions of 0.1 M 1-$IC_5H_{11}$ (a) and 0.1 M $CCl_4$ (b). Bands at 1950, 1937, and 1877 $cm^{-1}$ are due to starting materials. In (a) the bands at 1996 and 1781 $cm^{-1}$ are characteristic of $(\eta^5\text{-}C_5H_5)_2Fe(CO)_4$, that at 2039 $cm^{-1}$ is primarily due to $(\eta^5\text{-}C_5H_5)Mo(CO)_3I$, and that at 1910 $cm^{-1}$ is due to $(\eta^5\text{-}C_5H_5)Mo_2(CO)_6$. The band marked by * is a solvent absorption in (a) and (b). In (b) the band at 2003 $cm^{-1}$ is characteristic of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, that at 1977 $cm^{-1}$ is characteristic of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$, and the band at 2051 $cm^{-1}$ is due to both metal carbonyl chloride products; cf. Table V.

conditions we found essentially quantitative yields of $Co_2(CO)_8$.

The data in Table V allow some qualitative remarks on the relative reactivity of the two halocarbons and the four metal radicals. For the two halocarbons we found that $CCl_4$ is clearly the more reactive. This statement is supported by the fact that irradiation of the M-M' species in the benzene solutions of 0.1 M halocarbon gives more of the M-M products for 1-$IC_5H_{11}$ than for $CCl_4$. The reactivity of the 17e$^-$ radicals qualitatively follows the ordering[12] $(\eta^5\text{-}C_5H_5)W(CO)_3 > (\eta^5\text{-}C_5H_5)Mo(CO)_3 > (\eta^5\text{-}C_5H_5)Fe(CO)_2 > Co(CO)_4$. The data in Table V reinforce our earlier ordering. Under the conditions used, we have observed all four possible products for only $(\eta^5\text{-}C_5H_5)(CO)_3MoFe(CO)_2(\eta^5\text{-}C_5H_5)$ in the presence of 0.1 M 1-$IC_5H_{11}$. The data in Table V for this complex give a relative rate constant of 0.29 for the abstraction of iodine atoms by $Fe(CO)_2(\eta^5\text{-}C_5H_5)$ compared to $Mo(CO)_3(\eta^5\text{-}C_5H_5)$. Our earlier data[12] gave 0.28; the agreement is excellent. The absence of any $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ from irradiation of $(\eta^5\text{-}C_5H_5)(CO)_3WFe(CO)_2(\eta^5\text{-}C_5H_5)$ while substantial quantities of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ are found shows that the $W(CO)_3(\eta^5\text{-}C_5H_5)$ is more reactive than the $Fe(CO)_2(\eta^5\text{-}C_5H_5)$ toward 1-$IC_5H_{11}$. The general finding that $Co(CO)_4$ fragments efficiently couple suggests that it is the least reactive radical. The relative reactivities of $Mo(CO)_3(\eta^5\text{-}C_5H_5)$ and $W(CO)_3(\eta^5\text{-}C_5H_5)$ were assigned[12] on the basis of an irradiation of $(\eta^5\text{-}C_5H_5)_2MoW(CO)_6$. We have not yet completed detailed additional studies concerning heterodinuclear precursors to $Mn(CO)_5$ and $Re(CO)_5$, but our earlier findings place both of these as more reactive than any of the radicals studied here.

One final point requires explanation. The various precursors to a given fragment do not appear to give the same ratio of coupling to abstraction. For example, irradiation of $(\eta^5\text{-}C_5H_5)(CO)_3MoCo(CO)_4$ in 0.1 M $CCl_4$ gives some $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ and $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$, whereas $(\eta^5\text{-}C_5H_5)(CO)_3MoFe(CO)_2(\eta^5\text{-}C_5H_5)$ gives $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ as the only Mo-containing product. The apparent discrepancy is a consequence of several factors. First, the quantum yields for M–M′ scission in the two species may be different giving different rates of radical production. There do seem to be some experimentally significant differences among the complexes, Table IV. Further, we have made no effort to ensure constancy of the number of einsteins per time absorbed by the sample. This should give differences in coupling and abstraction, since this will cause variation in steady-state radical concentration. As pointed out earlier,[12] we have shown that $Mo(CO)_3(\eta^5\text{-}C_5H_5)$, independent of precursor, reacts to give a constant ratio of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ and $(\eta^5\text{-}C_5H_5)Mo(CO)_3I$ when the precursor is irradiated in the presence of a constant mixture of $CCl_4$ and $1\text{-}IC_5H_{11}$.

## Experimental Section

**Materials.** The $Co_2(CO)_8$ was obtained from Strem Chemicals Inc. and used after sublimation. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was obtained commercially and used after recrystallization. $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo, W) were synthesized by established routes for previous studies in this laboratory. The $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ compounds were synthesized as before[5a] and the $(\eta^5\text{-}C_5H_5)M(CO)_3I$ compounds were prepared in the same fashion, substituting a solution of $I_2$ in benzene for $CCl_4$. $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ (X = Cl, I) were gifts from Professor A. Davison's research group. $Co_3(CO)_9CCl$ was a gift from Professor D. Seyferth's research group. All solvents were of spectroscopic grade and used without purification, except benzene and the halocarbons which were reagent grade and purified by distillation (from Na/K for benzene). Elemental analyses were performed by Alfred Bernhardt.

**Spectra.** All electronic absorption spectra were obtained using a Cary 17 UV–vis–near-IR spectrophotometer. Low-temperature spectra of EPA solutions were recorded using a quartz liquid-nitrogen Dewar fitted with quartz optical flats for windows. All infrared spectra were obtained with a Perkin-Elmer 180 infrared spectrophotometer. Quantitative measurements were made in the linear-absorbance mode with a spectral resolution of 1–1.5 $cm^{-1}$ using matched 0.1- or 1.0-mm path length, amalgam-sealed NaCl cells obtained from Perkin-Elmer Corp. Melting points were determined with a Mel-Temp apparatus in sealed capillaries under argon and are corrected. $^1H$ NMR spectra were collected using a Varian T-60 instrument.

**Synthesis of $(\eta^5\text{-}C_5H_5)(CO)_3MCo(CO)_4$ (M = Mo, W).** The method of synthesis for both compounds is the same and can be illustrated by that for $(\eta^5\text{-}C_5H_5)(CO)_3MoCo(CO)_4$. A carbon monoxide purged solution of 0.496 g (1.01 mmol) of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ and 0.380 g (1.11 mmol) of $Co_2(CO)_8$ in 100 mL of benzene in a Vycor vessel was irradiated with a 550-W Hanovia medium-pressure Hg lamp with a broad-band UV filter (260–400 nm transmitted) until the IR spectrum showed that product formation had all but stopped (3–4 h). The solution was rotary evaporated to dryness (20 Torr, 40 °C). Some of the $Co_2(CO)_8$ sublimed out during this step. The solid was slurried with 50 mL of pentane and filtered to remove most of the $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ as a solid. The product was separated from the reactants by chromatography in the dark on grade I alumina. Unreacted $Co_2(CO)_8$ was eluted down the column with pentane, where it decomposed. The $(\eta^5\text{-}C_5H_5)(CO)_3MoCo(CO)_4$ was eluted with 15% $CH_2Cl_2$ in pentane (v/v) followed by $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$. The product was recrystallized from pentane and identified by IR and electronic spectral properties and photochemical behavior. The yield was 0.230 g (50%, based on $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ disappearance). The yield was 40% for the W–Co compound. The elemental analyses were satisfactory. Anal. Calcd for $(\eta^5\text{-}C_5H_5)(CO)_3MoCo(CO)_4$: C, 34.64; H, 1.21; O, 26.92. Found: C, 34.78; H, 1.32; O, 26.90. Anal. Calcd for $(\eta^5\text{-}C_5H_5)(CO)_3WCo(CO)_4$: C, 28.60; H, 1.00; O, 22.22. Found: C, 28.55; H, 1.01; O, 22.41. Other physical data: mp (sealed under Ar) Mo–Co 63–65 °C, W–Co 74.5–77 °C; $^1H$ NMR ($Me_4Si$ reference, $C_6D_6$ solution) Mo–Co $\tau$ 5.40, W–Co $\tau$ 5.38.

**Synthesis of $(\eta^5\text{-}C_5H_5)(CO)_3MoFe(CO)_2(\eta^5\text{-}C_5H_5)$.** The method was similar to that of the above complexes, except that an argon purge and a Pyrex filter were used. Reaction time was 45 min. Crude product was chromatographed twice on a grade II alumina column, eluting the product with hexane. The product was recrystallized from pentane. A satisfactory elemental analysis was obtained. Anal. Calcd: C, 42.69; H, 2.39; O, 18.96. Found: C, 42.42; H, 2.49; O, 18.83. Mp 205 °C (lit. 209 °C[18]); $^1H$ NMR ($Me_4Si$ reference, $C_6D_6$ solution) $\tau$ 5.17, 5.75 (1:1).

**Synthesis of $(\eta^5\text{-}C_5H_5)(CO)_3WFe(CO)_2(\eta^5\text{-}C_5H_5)$.** The method was similar to that for the $(\eta^5\text{-}C_5H_5)(CO)_3MCo(CO)_4$, except that an argon purge was used. The crude product was slurried with hexane and filtered to remove most of the $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ as solids. The solvent was stripped from the filtrate and the solid was redissolved in $CH_2Cl_2/C_6H_6$ and chromatographed on a grade I alumina column in the dark. Elution with $C_6H_6$ removed much of the $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$, and $CH_2Cl_2$ eluted the desired product. The $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ eluted very slowly. The fractions containing product also contained some of the $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ starting material. Repeated attempts to remove the residual starting material through chromatography on silica gel or grades I–III alumina using a variety of solvents, including pentane, hexane, isooctane, benzene, and dichloromethane, were unsuccessful. Repeated recrystallization from $CH_2Cl_2$/hexane reduced the content of $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ to 6.3 mol %, as determined by IR analysis in isooctane. All reactions were done using material of this purity and all extinction coefficients and quantum yields are corrected for the presence of the tungsten dimer. The elemental analysis was satisfactory. Anal. Calcd for 94% $(\eta^5\text{-}C_5H_5)(CO)_3WFe(CO)_2(\eta^5\text{-}C_5H_5)$, 6% $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$: C, 34.94; H, 1.95; O, 15.61. Found: C, 35.22; H, 2.03; O, 15.80. Other physical data: softens 145 °C, mp 220 °C dec; $^1H$ NMR ($Me_4Si$ reference, $C_6D_6$ solution) $\tau$ 5.23, 5.68 (1:1). Recently a thermal preparation of this compound was reported,[19] but the reported infrared spectrum indicates the presence of substantial amounts of impurity.

**Flash Photolysis of M–M′.** Degassed solutions of the M–M′ species ($1 \times 10^{-2}$ M) in benzene were flashed using a Xenon Corp. Model F-710 flash-photolysis apparatus as a light source. The disappearance of starting materials and appearance of products were monitored by IR spectroscopy.

**Photolysis of M–M′ in Solutions Containing RX.** For most experiments a solution of the M–M′ species ($10^{-2}$ M) in benzene with added 0.1 M halocarbon ($1\text{-}IC_5H_{11}$ or $CCl_4$) was purged with argon and loaded into an amalgam-sealed NaCl IR cell and sealed with Teflon stoppers. Photolysis of the solution in the cell with a GE Black Light (300–400 nm) produced changes which were monitored by IR spectroscopy.

For the quantum yield determinations, 3-mL-aliquot solutions of the M–M′ species $\sim 10^{-3}$ M in $CCl_4$ were placed in Pyrex test tubes (13 × 100 mm) with constrictions. The solutions were degassed in at least four freeze–pump–thaw cycles and hermetically sealed. The photolysis source was a merry-go-round[20] equipped with a 550-W Hanovia medium-pressure Hg lamp filtered with Corning glass filters to isolate the 366-nm Hg emission line. Ferrioxalate actinometry[21] was performed for each experiment to measure the light intensity. Disappearance of the M–M′ complex and appearance of products was monitored by IR spectroscopy. The extinction coefficients for infrared bands in the carbonyl stretching region were determined from solutions of authentic samples of reactants and products at known concentrations in cells of known path length. Quantum yields are reported for <15% conversion to avoid secondary photolysis.

**Analyses by Infrared Spectroscopy.** Flash-photolysis and continuous-irradiation-induced reactions were all monitored by infrared spectral changes in the CO stretching region. Authentic samples of all starting materials and products were used to measure the bands and their absorptivities in the solvent of interest. In most cases the starting materials and products had at least one distinct, nonoverlapping band which could be used for quantitative analysis of each metal carbonyl component of the solution (cf. Figures 1–3 and Table II). Within experimental error, all M and M′ fragments from M–M′ could be accounted for by the analysis, Tables III–V. The experimental error for the yields was ±15%.

**Acknowledgment.** We thank the National Science Foundation for support of this research and for a graduate fellowship to H.B.A.

**Registry No.** $(\eta^5\text{-}C_5H_5)(CO)_3MoCo(CO)_4$, 62015-65-0; $(\eta^5\text{-}C_5H_5)(CO)_3WCo(CO)_4$, 62015-64-9; $(\eta^5\text{-}C_5H_5)(CO)_3MoFe(CO)_2(\eta^5\text{-}C_5H_5)$, 12130-13-1; $(\eta^5\text{-}C_5H_5)(CO)_3WFe(CO)_2(\eta^5\text{-}C_5H_5)$, 64041-01-6; $[(\eta^5\text{-}C_5H_5)(Mo(CO)_3]_2$, 12091-64-4; $Co_2(CO)_8$, 10210-68-1; $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$, 12128-23-3; $(\eta^5\text{-}C_5H_5)Mo(CO)_3I$, 12287-61-5; $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$, 12566-66-4; $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$, 12128-24-4; $(\eta^5\text{-}C_5H_5)W(CO)_3I$, 31870-69-6; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12154-95-9; $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, 12107-04-9; $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, 12078-28-3; $Co_3(CO)_9CCl$, 19512-60-8.

## References and Notes

(1) Dreyfus Teacher-Scholar grant recipient, 1975–1980.

(2) (a) M. Wrighton and D. Bredesen, *J. Organomet. Chem.*, **50**, C35 (1973); (b) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 2065 (1975).

(3) A. Hudson, M. F. Lappert, and B. K. Nicholson, *J. Chem. Soc., Dalton Trans.*, 551 (1977).

(4) A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 966 (1974).

(5) (a) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 4246 (1975); (b) D. S. Ginley and M. S. Wrighton, *ibid.*, **97**, 4908 (1975); (c) D. L. Morse and M. S. Wrighton, *ibid.*, **98**, 3931 (1976).

(6) (a) C. Giannotti and G. Merle, *J. Organomet. Chem.*, **105**, 97 (1976); (b) R. M. Laine and P. C. Ford, *Inorg. Chem.*, **16**, 388 (1977).

(7) J. L. Hughey IV, C. R. Bock, and T. J. Meyer, *J. Am. Chem. Soc.*, **97**, 4440 (1975).

(8) J. L. Hughey IV, C. P. Anderson, and T. J. Meyer, *J. Organomet. Chem.*, **125**, C49 (1977).

(9) (a) B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.*, **97**, 947, 3260 (1975); **99**, 2527 (1977); (b) M. Absi-Halabi and T. L. Brown, *ibid.*, **99**, 2982 (1977).

(10) D. M. Allen, A. Cox, T. J. Kemp, Q. Sultana, and R. B. Pitts, *J. Chem. Soc., Dalton Trans.*, 1189 (1976).

(11) A. R. Burkett, T. J. Meyer, and D. G. Whitten, *J. Organomet. Chem.*, **67**, 67 (1974).

(12) H. B. Abrahamson and M. S. Wrighton, *J. Am. Chem. Soc.*, **99**, 5510 (1977).

(13) (a) R. A. Levenson, H. B. Gray, and G. P. Caesar, *J. Am. Chem. Soc.*, **92**, 3653 (1970); (b) R. A. Levenson and H. B. Gray, *ibid.*, **97**, 6042 (1975); (c) D. C. Harris and H. B. Gray, *ibid.*, **97**, 3073 (1975).

(14) H. B. Abrahamson, C. C. Frazier, D. S. Ginley, H. B. Gray, J. Lilienthal, D. R. Tyler, and M. S. Wrighton, *Inorg. Chem.*, **16**, 1554 (1977).

(15) D. S. Ginley, Ph.D. Thesis, MIT, 1976.

(16) D. C. Harris and H. B. Gray, *Inorg. Chem.*, **14**, 1215 (1975).

(17) M. C. Palazzotto and M. S. Wrighton, to be submitted for publication.

(18) R. B. King, P. M. Treichel, and F. G. A. Stone, *Chem. Ind. (London)*, 747 (1961).

(19) V. N. Pandey, *Inorg. Chim. Acta*, **23**, L26 (1977).

(20) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

(21) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

---

Contribution from the Department of Chemistry,
University of Western Ontario, London, Ontario, Canada

# Shake-up Satellite Structure in the X-Ray Photoelectron Spectra (ESCA) of Metal Hexacarbonyls

G. MICHAEL BANCROFT,* BRIAN D. BOYD, and DAVID K. CREBER

*Received September 8, 1977*

Core-level (C 1s, O 1s, Cr 2p, Mo 3d, and W 4f) ESCA data have been recorded for $M(CO)_6$ (M = Cr, Mo, W) compounds in the gas phase using Mg K$\alpha$ and Al K$\alpha$ radiation. All levels show a number of satellites which are attributed to electron shake-up. For example, the O 1s spectrum of $Mo(CO)_6$ shows satellites at 5.4, 7.0, 9.8, 14.9, and 16.4 eV from the primary photoline. Only the first of these peaks has been seen in previous studies. By use of electronic spectra and molecular orbital calculations, the satellites have been tentatively assigned. For example, the most intense O 1s satellite at 5.4 eV has been assigned to the $2t_{2g} \rightarrow 3t_{2g}$ transition, which is predominantly a metal d → ligand $\pi^*$ charge-transfer transition. The same transition is responsible for the 5.6- and 5.1-eV satellites on the C 1s and Mo 3d levels, respectively. A similar satellite is also seen on the metal and ligand levels in the Cr and W compounds, and the energy of this transition varies in the sequence Cr < Mo < W. The considerable potential of these satellites for obtaining molecular orbital information is discussed.

## Introduction

Although chemical interest in x-ray photoelectron spectroscopy (or ESCA) has been largely directed toward the chemical shift parameter,[1,2] recent reviews[3,4] have drawn attention to the large number of studies on the small shake-up satellites on the low kinetic energy side of many primary photolines. These shake-up satellites are of considerable potential importance to the coordination chemist, as the shake-up positions are related to the energy difference between filled and unfilled molecular orbitals. As well as this energy difference, the intensity of the satellites has been used to determine the extent of covalency in metal–ligand[5,6] bonds. In transition-metal complexes,[3,4] one satellite is normally observed on the metal levels only, and these satellites are only common in first-row transition-metal complexes.[4] Only in transition-metal carbonyls and acetonates[3] have satellites been observed on ligand levels. In particular, the volatile group 6B metal hexacarbonyls $M(CO)_6$ have been studied extensively for chemical shift variations in the solid state (M = Cr, Mo, W)[7-11] and in the gas phase (M = Cr).[12] Shake-up structure has also been studied in the solid-state spectra.[11,13-15] In each shake-up study, only one intense shake-up peak (~30% of the intensity of the main line) has been observed in each of the C 1s and O 1s spectra at about 5.4 eV from the primary line. This peak has been assigned to a metal → ligand* ($M \rightarrow L^*$) charge-transfer transition.[14] There is one report[15] of an uncharacterized shake-up satellite on the Cr 2p level of $Cr(CO)_6$. Also, satellite structure is evident in published spectra of the Mo 3d level in $Mo(CO)_6$[14] and the W 4f level in $W(CO)_6$.[8,14] These latter two examples appear to be the only known examples of the occurrence of metal shake-up peaks in the second- and third-row transition-metal series.[4]

Recent ground-state molecular orbital[16,17] calculations strongly suggested that many shake-up transitions were possible in these compounds and that a number of satellites should be seen in the ESCA. Because the above shake-up spectra were recorded using condensed solids, rather broad primary peaks were usually obtained. In addition, the spectra

0020-1669/78/1317-1008$01.00/0 © 1978 American Chemical Society