

propriate quenching agent was added as a solution (for anions, as its sodium salt) in a few milliliters of water. A five- to tenfold excess of quenching agent was generally used.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this research. M.T.M. thanks the National Science Foundation for support through a predoctoral fellowship. The assistance of Professor S. Smith in conducting the stopped-flow measurements and Mr. Larry White and Professor Linn Belford with ESR spectral simulations is gratefully acknowledged.

References and Notes

- (1) L. F. Lindov and D. H. Busch, *Prep. Inorg. React.*, **6**, 1 (1971); D. H. Busch, *Helv. Chim. Acta, Fasciculus Extraordinarius Alfred Werner*, 174 (1967); D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Adv. Chem. Ser.*, No. 100, 44 (1971).
- (2) (a) E. S. Gore and D. H. Busch, *Inorg. Chem.*, **12**, 1 (1973); (b) E. K. Barefield and D. H. Busch, *Chem. Commun.*, 523 (1970); (c) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **8**, 1611 (1969); (d) N. F. Curtis and D. F. Cook, *Chem. Commun.*, 962 (1967).
- (3) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **10**, 463 (1971).
- (4) M. O. Kestner and A. L. Allred, *J. Am. Chem. Soc.*, **94**, 7189 (1972).
- (5) M. T. Mocella and E. K. Barefield, *Inorg. Chem.*, **12**, 2829 (1973).
- (6) (a) V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 207 (1972); (b) V. L. Goedken and D. H. Busch, *J. Am. Chem. Soc.*, **94**, 7355 (1972).
- (7) (a) N. F. Curtis, *Chem. Commun.*, 881 (1966); (b) E. G. Vassian and R. K. Murmann, *Inorg. Chem.*, **6**, 2043 (1967); (c) E. K. Barefield, F. V. Lovecchio, N. E. Tokel, E. Ochiai, and D. H. Busch, *Inorg. Chem.*, **11**, 283 (1972).
- (8) W. R. McWhinnie, J. D. Miller, J. B. Watt and D. Y. Waddan, *Chem. Commun.*, 629 (1971); B. C. Lane, J. E. Lester, and F. Basolo, *J. Chem. Soc., Chem. Commun.*, 207 (1972).
- (9) C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957, p 398; W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., 1966, p 288.
- (10) H. I. Chum and P. Krumholz, *Inorg. Chem.*, **13**, 519 (1974).
- (11) E. S. Gore and D. H. Busch, *Inorg. Chem.*, **12**, 1 (1973).
- (12) B. R. McGarvey, *Transition Met. Chem.*, **3**, 98 (1966).
- (13) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance", Harper and Row, New York, N.Y., 1967, p 79.
- (14) W. C. Danen and T. T. Kensler, *J. Am. Chem. Soc.*, **92**, 5235 (1970).
- (15) V. L. Goedken and D. H. Busch, *Inorg. Chem.*, **10**, 2679 (1971).
- (16) N. J. Turro, *Chem. Eng. News*, **45** (18), 94 (1967).
- (17) F. A. Cotton and G. F. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., 1972, p 179.
- (18) M. Anbar, *Adv. Chem. Ser.*, No. 49, 129 (1965).
- (19) A. McAuley, *Coord. Chem. Rev.*, **5**, 245 (1970).
- (20) For example, J. Hill, A. McAuley, and W. F. Pickering, *Chem. Commun.*, 573 (1967); T. J. Conocchioli, G. H. Nancollas, and N. Sutin, *Inorg. Chem.*, **5**, 1 (1966).
- (21) For example, A. A. Clifford and W. A. Waters, *J. Chem. Soc.*, 2796 (1965); E. L. King and M. L. Pendow, *J. Am. Chem. Soc.*, **75**, 3063 (1953); a number of other examples are cited in the bibliography to ref 19.
- (22) J. E. French and H. Taube, *J. Am. Chem. Soc.*, **91**, 6951 (1969).
- (23) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution", Academic Press, New York, N.Y., 1970, Chapter IV.
- (24) J. Siegel and T. N. Armor, *J. Am. Chem. Soc.*, **96**, 4102 (1974).
- (25) N. S. Rowan, Z. Hoffman, and R. M. Milburn, *J. Am. Chem. Soc.*, **96**, 6060 (1974).
- (26) E. O. Sherman, Jr., and D. C. Olson, *Anal. Chem.*, **40**, 1174 (1968).
- (27) N. F. Curtis, *J. Chem. Soc. C*, 1979 (1967).
- (28) E. K. Barefield, *Inorg. Chem.*, **11**, 2273 (1972); E. K. Barefield, F. Wagner, A. W. Herlinger, and A. R. Dahl, *Inorg. Synth.* **16** (1975).
- (29) G. Brauer, "Handbook of Preparative Inorganic Chemistry", Vol. 1, 2nd ed, Academic Press, New York, N.Y., 1963, p. 320.
- (30) E. K. Barefield, *J. Chem. Educ.*, **50**, 697 (1973).

Photochemistry of Metal–Metal Bonded Complexes. III. Photoreactivity of Hexacarbonylbis(η^5 -cyclopentadienyl)dimolybdenum(I) and -ditungsten(I)

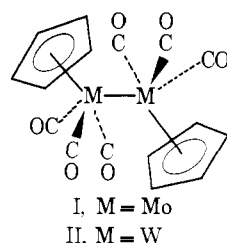
Mark S. Wrighton* and David S. Ginley

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received October 7, 1974

Abstract: The photolysis of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}, \text{W}$) in solution at 25° leads to efficient homolytic M–M bond cleavage. Photolysis in CCl_4 yields two molecules of the corresponding $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$ per molecule of the M–M bonded species with quantum efficiency for dimer disappearance in the range 0.12–0.45 depending on M and the photolysis wavelength. Simultaneous photolysis of $\text{M}'_2(\text{CO})_{10}$ ($\text{M}' = \text{Mn}, \text{Re}$) and $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ yields $(\text{OC})_5\text{M}'\text{M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ complexes with good chemical yield. The photochemistry is discussed in terms of lowest excited states involving the population of an orbital which is σ -antibonding with respect to the M–M bond.

The photolysis of Mn and Re carbonyls containing direct metal–metal bonds was recently shown to result in homolytic cleavage of the metal–metal bond.^{1–3} The photogenerated paramagnetic intermediates $\text{M}(\text{CO})_5$ ($\text{M} = \text{Mn}, \text{Re}$) have some reactivity patterns in common with their isoelectronic analog $\text{Co}(\text{CN})_5^{3-}$, and these d^7 , 17-electron molecules react with halogens and alkyl halides apparently via a free radical mechanism.^{1–4} Other metal carbonyls aside from Mn and Re have received some study⁵ with respect to metal–metal bond cleavage and among these is $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$ (I), which was shown⁶ to undergo efficient disproportionation upon photolysis in acetone solutions of Cl^- . Earlier work⁷ also provides some evidence for a net heterolytic cleavage of the Mo–Mo bond upon prolonged photolysis in benzene solutions of PPh_3 . Other work-

ers claim that simple CO substitution products arise from the photolysis of I in the presence of nucleophiles such as $\text{P}(\text{OPh})_3$ ⁸ or PPh_3 .⁹ There seems to be no reported detailed studies of the photoreactivity of the third-row analog to I, $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_6$ (II). The structures of I and II are as shown below.¹⁰



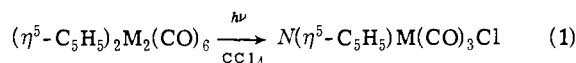
Heterolytic cleavage of the metal-metal bond in I or II should yield the known carbonyl anion $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3^-$ which can be isolated as the sodium, lithium, or potassium salt.¹¹ The reactions of metal carbonyl anions, such as $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3^-$ have been well studied¹² and are of some importance in organometallic synthesis. Homolytic cleavage of the M-M bond in I or II would yield the neutral species, $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3$, which is paramagnetic, but no well-characterized electronic analogs are known. The differences in the chemistry of $\text{Re}(\text{CO})_5^{1-2}$ and $\text{Re}(\text{CO})_5^{1-3}$ are substantial, thus we may expect some differences between the two possible M-M cleavage products of I and II. The neutral $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3$ can be viewed as a d^5 , 17-electron intermediate in contrast to $\text{Re}(\text{CO})_5$, $\text{Mn}(\text{CO})_5$, and $\text{Co}(\text{CN})_5^{3-}$ which are all 17-electron species but of the d^7 electronic configuration. Though this electronic distinction exists, the types of $\text{XM}(\text{CO})_5$ ($\text{M} = \text{Re}, \text{Mn}$) and $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{X}$ ($\text{M} = \text{Mo}, \text{W}$) compounds that exist telegraph the possibility that the d^7 and d^5 , 17-electron intermediates may participate in similar chemical reactions. In this paper we report a detailed investigation of the photochemical reactivity of both I and II. The results add substantially to the current understanding⁶⁻⁹ of the photoprocesses in these complexes.

Results

a. Spectra of Complexes. The uv-visible absorption spectra of I and II are shown in Figure 1 at 298 and 77°K in EPA. Absorption band maxima and molar extinction coefficients for I and II and for $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$ ($\text{M} = \text{Mo}, \text{W}$) are listed in Table I for 298°K measurements. The data show that the low energy region of the absorption spectra of I and II are very similar, consisting of two, well-defined bands which are not particularly sensitive to solvent or temperature. The lowest absorption (λ_{max} near 500 nm; $\epsilon \approx 1800 \text{ l. mol}^{-1} \text{ cm}^{-1}$) gives rise to the intense red-purple color of I and II, and the second absorption falls in the near-uv and is very intense ($\epsilon \approx 18,000 \text{ l. mol}^{-1} \text{ cm}^{-1}$). The mononuclear species $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$ ($\text{M} = \text{Mo}, \text{W}$) are similar to each other exhibiting a relatively weak ($\epsilon \approx 400 \text{ l. mol}^{-1} \text{ cm}^{-1}$) visible absorption maximizing somewhat to the blue compared to the corresponding metal-metal bonded complexes giving their yellow-orange appearance. The $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$ complexes exhibit no near-uv transition corresponding to the very intense band found in I and II.

Infrared spectroscopy has served as a tool for the quantitative analyses of the photoreactions of I and II. Infrared absorption maxima in the CO stretching region and their molar extinction coefficients are summarized in Table II for several complexes. The band positions that we find correspond closely to those previously reported for these complexes.¹³⁻¹⁵

b. Photochemistry of I and II in CCl_4 . The near-uv and visible photolysis of I or II in degassed CCl_4 solution proceeds according to reaction 1. The stoichiometric coefficient



N has been determined from appearance of the product measured by both uv-visible and ir spectral changes shown in Figures 2 and 3 for photolysis of I and II, respectively. Reaction quantum yields at 366, 405, and 550 nm and the experimental value of N are given in Table III. As shown, the quantum yields are fairly high upon photolysis in the tail of lowest energy absorption (550 nm) or in the intense near-uv absorption (366 nm), and the value of N is very near 2.0 for both I and II. The product indicated in reaction 1 is thus the sole photoproduct obtained, and its identity has

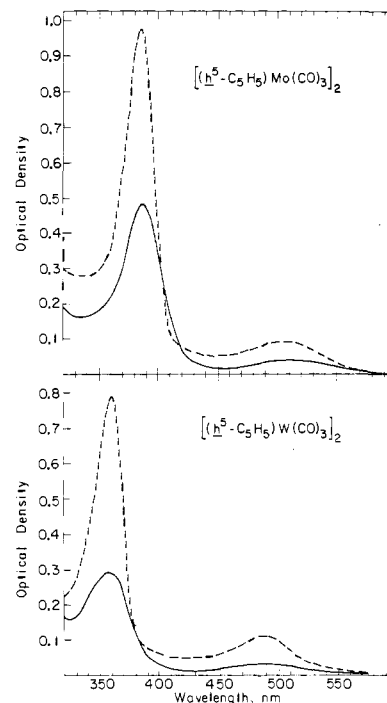


Figure 1. Electronic absorption spectra of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}, \text{W}$) in EPA at 298°K (—) and 77°K (---). Spectral changes upon cooling are not corrected for solvent contraction. Molar absorptivities at 298°K are given in Table I.

Table I. Electronic Spectral Features of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{X}$ Complexes at 25°

X	M	Solvent	Band maxima, nm (ϵ)	
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3$	Mo	CCl_4	515 (1860)	389 (21,000)
		C_6H_6	513 (1620)	390 (19,700)
		THF	509 (1730)	388 (18,600)
		CH_3OH	505 (1610)	385 (17,400)
		Acetone	503 (1620)	384 (17,200)
		CH_3CN	503 (1610)	384 (16,900)
		CH_2Cl_2	510 (1790)	388 (20,000)
$(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3$	W	Isooctane	512 (1720)	388 (20,400)
		EPA	508 (-)	387 (-)
		CCl_4	493 (2450)	362 (20,200)
		EPA	492 (-)	358 (-)
Cl	Mo	CCl_4	475 (389)	320 (sh)
		CH_2Cl_2	475 (-)	320 (sh)
		Acetone	473 (-)	330 (-)
Cl	W	CCl_4	460 (510)	315 (2200)

Table II. Ir Absorption Data for $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{X}$ Complexes at 25°

X	Solvent	M	Bands, cm^{-1} (ϵ)
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3$	CCl_4	Mo	1960 (9800), 1914 (6400)
	Isooctane	Mo	1960 (7500), 1915 (4900)
$(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3$	CCl_4	W	1955 (11,050), 1908 (6400)
	Isooctane	W	1958 (9800), 1910 (7700)
$\text{Mn}(\text{CO})_5$	Isooctane	Mo	2082 (4100), 2021 (2200), 2012 (w), 1996 (11,600), 1959 (sh), 1920 (1300), 1905 (2800)
		W	2087 (3950), 2026 (2200), 1991 (9950), 1973 (6440), 1908 (1500), 1890 (3300)
Cl	CCl_4	Mo	2055 (1700), 1983 (2400)
	CCl_4	W	2053 (2800), 1968 (4600), 1947 (2150)
$\text{Re}(\text{CO})_5$	Isooctane	W	2111 (1860), 2000 (6880), 1968 (4440), 1875 (3150)
$\text{Re}(\text{CO})_5$	Isooctane	Mo	2106 (1600), 2038 (900), 1998 (3860), 1976 (3790), 1903 (800)

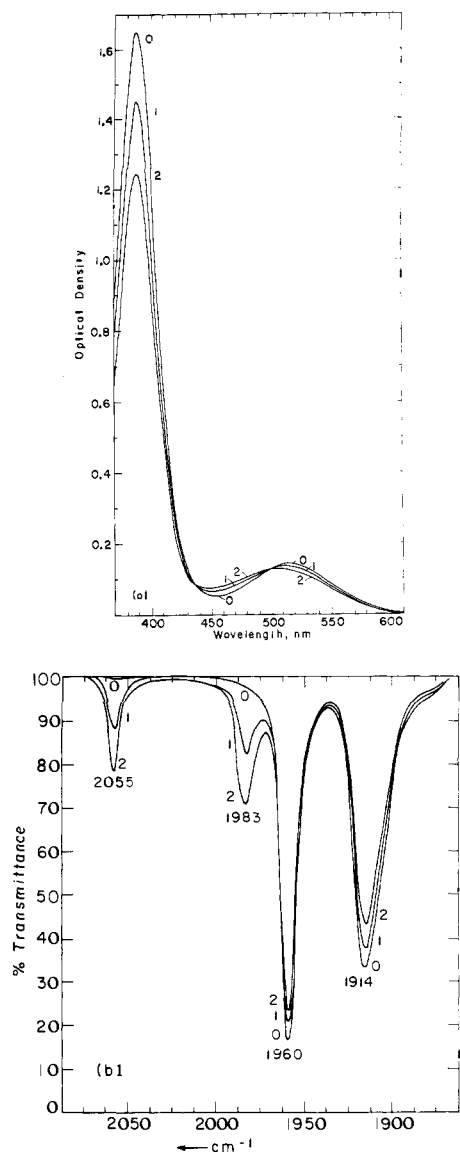


Figure 2. (a) Electronic spectral and (b) ir spectral changes accompanying the 366-nm photolysis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ initially $7.9 \times 10^{-4} M$ in degassed CCl_4 solution at 25° . Curve 0, 1, and 2 are after 0, 10, and 20 min of photolysis at 7.13×10^{-8} einstein/min. The ir spectra were taken without dilution, but the uv-visible was recorded after dilution by a factor of 10 with CCl_4 .

Table III. Photoreaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_6$ in CCl_4 ^a

M	Photolysis		Φ_{dis}^b	Φ_{appear}^c	N^d
	λ , nm				
Mo	550		0.35	0.77	2.20
	405		0.42	0.94	2.25
	366		0.45	1.04	2.30
W	550		0.12	0.25	2.05
	366		0.21	0.41	1.93

^a At 298°K ; degassed solutions. ^b Quantum yield for disappearance of starting complex. ^c Quantum yield for appearance of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$. ^d Ratio of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$ appearance to $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_6$ disappearance.

been unequivocally established by a combination of ir spectra and elemental analyses.

c. Photochemistry of I and II in the Presence of Ph_3CCl and PhCH_2Cl . Photolysis at 550 nm of I or II in degassed solutions containing 0.1 M Ph_3CCl yields the $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$ and the ESR detectable $\text{Ph}_3\text{C}\cdot$ free radical. Quantitative analysis of the reaction of I shows that two

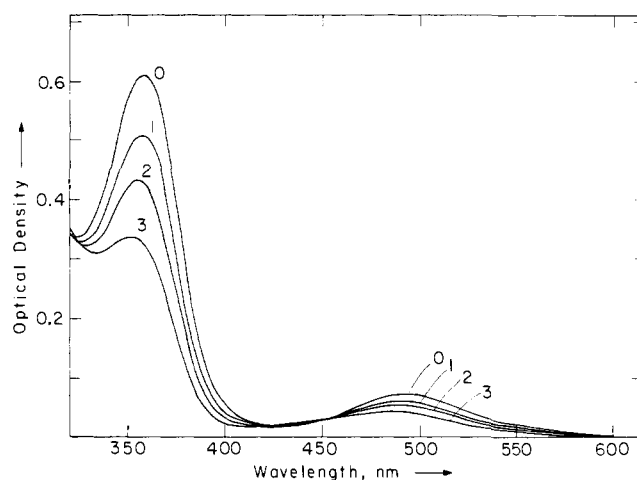
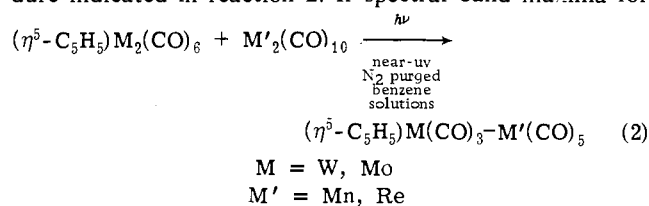


Figure 3. Electronic spectral changes accompanying the 366-nm photolysis of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$ under conditions comparable to those given in Figure 2. Curves 0, 1, 2, and 3 are sequential photolysis times.

molecules of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Cl}$ appear per molecule of I which disappears. Near-uv photolysis of I or II in the presence of 0.1 M PhCH_2Cl again leads essentially quantitatively to $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$ and a $\sim 90\%$ chemical yield of $\text{PhCH}_2\text{CH}_2\text{Ph}$. In both of these cases the quantum yield for $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$ formation is not substantially different from reactions in CCl_4 .

d. Flash Photolysis of Mixtures of I or II with $\text{M}'_2(\text{CO})_{10}$.

Either continuous or flash photolysis of degassed isooctane solutions of I or II and $\text{M}'_2(\text{CO})_{10}$ ($\text{M}' = \text{Mn, Re}$) yield mixed metal-metal bonded complexes. We have synthesized all four possible M-M' species according to the procedure indicated in reaction 2. Ir spectral band maxima for



these known complexes are as found in the literature.¹⁵ Quantitative analysis of several flash photolysis experiments are given in Table IV. The data show that extremely good yields of the M-M' products obtain based on the amount of the homonuclear species which disappear. The ir spectral changes accompanying flash photolysis of II and $\text{Mn}_2(\text{CO})_{10}$ are shown in Figure 4. Quantum yield measurements for reaction 2 are very complicated as we find that no M-M' species form if only one of the homonuclear starting materials is photolyzed. For example, 550 nm photolysis of I or II in the presence of $\text{Mn}_2(\text{CO})_{10}$ leads to no disappearance of the $\text{Mn}_2(\text{CO})_{10}$ which does not absorb at this wavelength. We can say, though, that when broad band (300–380 nm) near-uv photolysis is carried out (where both components absorb) the reactions occur smoothly and with seemingly good quantum efficiency.

Discussion

The photolysis of I and II in the presence of chlorine donors and $\text{M}'_2(\text{CO})_{10}$ ($\text{M}' = \text{Mn, Re}$) results in products which are only consistent with homolytic metal-metal bond cleavage in I or II subsequent to electronic excitation, reaction 3. This follows collectively from (1) the clean stoichi-

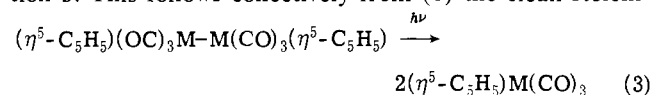


Table IV. Photoinduced Cross Coupling Reactions of Metal–Metal Bonded Complexes^a

Starting mixture (mol)	No. of flashes ^b	No. of mol reacted	Product (no. of moles formed)
Mn ₂ (CO) ₁₀ (8.61 × 10 ⁻⁷) + [(η ⁵ -C ₅ H ₅)W(CO) ₃] ₂ (2.33 × 10 ⁻⁷)	1	0.67 × 10 ⁻⁷ 0.61 × 10 ⁻⁷	(OC) ₅ Mn–W(CO) ₃ (η ⁵ -C ₅ H ₅) (1.52 × 10 ⁻⁷)
Mn ₂ (CO) ₁₀ (8.61 × 10 ⁻⁷) + [(η ⁵ -C ₅ H ₅)W(CO) ₃] ₂ (2.33 × 10 ⁻⁷)	3	0.99 × 10 ⁻⁷ 1.21 × 10 ⁻⁷	(OC) ₅ Mn–W(CO) ₃ (η ⁵ -C ₅ H ₅) (2.42 × 10 ⁻⁷)
Mn ₂ (CO) ₁₀ (7.27 × 10 ⁻⁶) + [(η ⁵ -C ₅ H ₅)Mo(CO) ₃] ₂ (1.51 × 10 ⁻⁶)	5	0.45 × 10 ⁻⁶ 0.82 × 10 ⁻⁶	(OC) ₅ Mn–Mo(CO) ₃ (η ⁵ -C ₅ H ₅) (1.38 × 10 ⁻⁶)
Mn ₂ (CO) ₁₀ (5.80 × 10 ⁻⁷) + [(η ⁵ -C ₅ H ₅)Mo(CO) ₃] ₂ (6.64 × 10 ⁻⁷)	3	1.54 × 10 ⁻⁷ 1.81 × 10 ⁻⁷	(OC) ₅ Mn–Mo(CO) ₃ (η ⁵ -C ₅ H ₅) (2.99 × 10 ⁻⁷)
Re ₂ (CO) ₁₀ (6.74 × 10 ⁻⁷) + [(η ⁵ -C ₅ H ₅)Mo(CO) ₃] ₂ (7.00 × 10 ⁻⁷)	3	1.94 × 10 ⁻⁷ 2.70 × 10 ⁻⁷	(OC) ₅ Re–Mo(CO) ₃ (η ⁵ -C ₅ H ₅) (2.25 × 10 ⁻⁷)
Re ₂ (CO) ₁₀ (7.34 × 10 ⁻⁷) + [(η ⁵ -C ₅ H ₅)W(CO) ₃] ₂ (5.38 × 10 ⁻⁷)	3	2.20 × 10 ⁻⁷ 1.54 × 10 ⁻⁷	(OC) ₅ Re–W(CO) ₃ (η ⁵ -C ₅ H ₅) (0.83 × 10 ⁻⁷)

^a In 3.0 ml of degassed isooctane solutions; analysis by ir. ^b Photolysis flash at 300–400 J using Xenon Corp. flash photolysis apparatus.

ometry with respect to (η⁵-C₅H₅)M(CO)₃Cl formation, (2) the observation of Ph₃C· radicals when Ph₃CCl is the chlorine donor, (3) high yields of bibenzyl when PhCH₂Cl is the chlorine donor, and (4) the efficient appearance of M–M' products which likely arise from coupling of (η⁵-C₅H₅)M(CO)₃ and M'(CO)₅. The photoproduction of the intermediates indicated in (3) has a very high quantum efficiency (Table III), but recombination likely accounts for some fraction of the primary photoproducts. The data here rule out heterolytic cleavage of the metal–metal bond in I or II as the primary excited state decay path. In particular, the anionic intermediate should not give (η⁵-C₅H₅)M(CO)₃Cl upon photolysis of I or II in the presence of PhCH₂Cl,¹² nor would anions and cations from I or II yield efficient cross-coupled M–M' products since it has already been shown that M'₂(CO)₁₀ cleaves homolytically^{1–3} following photoexcitation.

The fact that homolytic cleavage of the M–M bond obtains is seemingly inconsistent with previous reports^{6,7} of heterolytic cleavage. Two possibilities can account for this discrepancy. First, the primary photoprocess could depend on the environment. This, however, seems unlikely since the electronic spectra are influenced only to a small extent by variation in solvent. A more reasonable rationale rests with the possibility that the photogenerated metal radicals undergo secondary thermal reaction with components in solution. With regard to the simple CO photosubstitution products^{8,9} obtained from I, we can say that prompt CO dissociation is only a very minor component of the excited state decay since quantum yields for (η⁵-C₅H₅)M(CO)₃Cl formation are high and the stoichiometry is very clean. Prompt CO dissociation from I or II would yield a coordinatively unsaturated species likely capable of reacting destructively with CCl₄. Thus, the likely mechanism for CO substitution involves (1) cleavage of the M–M bond, (2) thermal substitution of CO in the metal radical by the entering group, and (3) re-formation of the M–M by coupling of two radicals. A similar mechanism was recently proposed² for PPh₃ photosubstitution for CO in Mn₂(CO)₁₀. Further investigation of the chemistry of the photogenerated intermediates from I and II will be reported subsequently. At the present time it appears that the d⁵, 17-electron (η⁵-C₅H₅)M(CO)₃ intermediates have some chemical properties in common with the d⁷, 17-electron intermediates.^{1–4}

The symmetry of species I and II is very low and consequently we cannot, at this time, rigorously discuss their electronic structure. However, the photochemistry of I and II and their absorption spectra have some features in common with the M'₂(CO)₁₀ (M' = Mn, Re) and the Mn₂(CO)_n(PPh₃)_{10–n} systems.^{1–3} First, all of the systems undergo homolytic metal–metal bond cleavage upon pho-

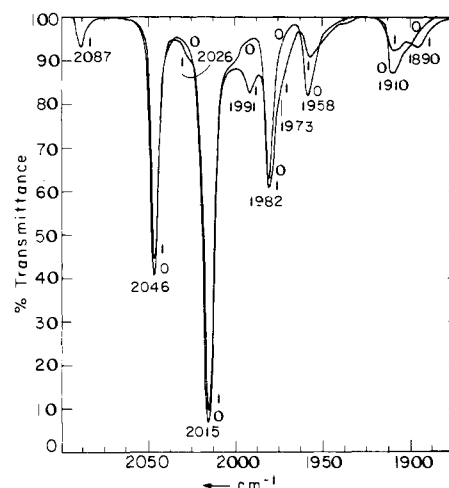
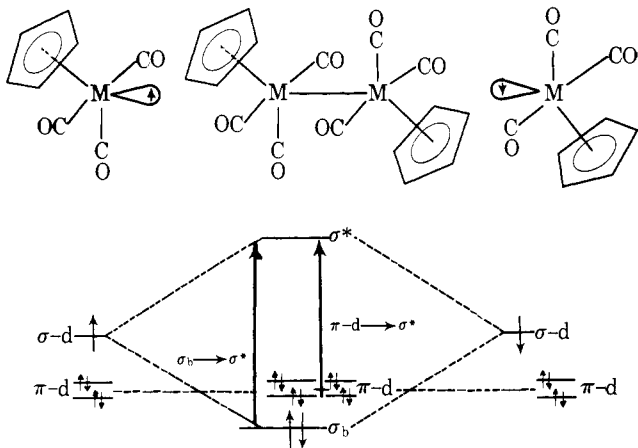


Figure 4. Infrared spectral changes accompanying flash photolysis of Mn₂(CO)₁₀ (2.87 × 10⁻⁴ M) and [(η⁵-C₅H₅)W(CO)₃]₂ (0.78 × 10⁻⁴ M) in degassed isooctane solutions in Pyrex ampules. Curve 0 is the initial spectrum and curve 1 is after three flashes at 300 J using the Xenon flash photolysis apparatus. The bands at 2046, 2015, and 1982 cm⁻¹ are due to Mn₂(CO)₁₀, bands at 1958 and 1910 cm⁻¹ are due to [(η⁵-C₅H₅)W(CO)₃]₂, and bands at 2087, 2026, 1991, 1973, and 1890 cm⁻¹ are due to (OC)₅MnW(CO)₃(η⁵-C₅H₅).

toexcitation. This calls for an accessible electronically excited state in the metal–metal bonded complexes which has a weaker metal–metal bond than in the ground electronic state. Second, all of the molecules mentioned have a very intense, fairly narrow, near-uv absorption which seems to have no analog in (η⁵-C₅H₅)M(CO)₃Cl (M = Mo, W) or in M'(CO)₅Cl (M' = Mn, Re). Finally, every Mn–Mn bonded complex and I and II exhibit a lower energy, lower intensity (by about a factor of 10 in each case) absorption band compared to the intense, sharp absorption band in the near-uv. The lower intensity band does seem to have a counterpart in M'(CO)₅Cl and (η⁵-C₅H₅)M(CO)₃Cl. These results of photon absorption suggest some common assignments for the spectra of I and II and for M'₂(CO)₁₀: the intense near-uv band, ε ≈ 20,000 l. mol⁻¹ cm⁻¹, is associated with a one-electron transition involving depopulation of a σ-bonding orbital for the M'–M' interaction in M'₂(CO)₁₀ and population of the corresponding σ-antibonding level.¹⁶ We adopt this formalism for I and II. The lower energy band is a one-electron transition associated with depopulation of the π-d(d_{xy}, d_{xz}, or d_{yz}) orbitals involved in M–CO π-bonding in M'₂(CO)₁₀ and population of the M'–M' σ-antibonding level. Such a transition would still be present in M'(CO)₅Cl since it is essentially a ligand-field (LF) transition (π-d → d_z). For I and II the low energy band is similarly ascribed

Scheme I



to this type of LF transition. Since the symmetry is so low, a simple one-electron diagram involving use of the basis set d_{xz} , d_{yz} , d_{xy} , d_{z^2} , $d_{x^2-y^2}$ orbitals is not illuminating. However, a posteriori we can assemble a reasonable one-electron energy level scheme as shown in Scheme I. Now, the monomer $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3$ units are of d^5 electronic configuration and the $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ can be viewed as having a d^4 configuration at each metal and a two-electron M-M σ -bond with the σ -orbital being the result of the overlap of a monomer d orbital of σ symmetry with respect to the resulting M-M bond. The heavy arrows in Scheme I indicate the two types of low lying electronic transitions each which will result in a weakened M-M bond. One final piece of experimental data is consistent with the above model and it concerns the wavelength effect for the M-M bond cleavage quantum yield (Table III). Though the effect is modest, we do see that 550 nm excitation ($\pi\text{-d} \rightarrow \sigma^*$) gives a smaller quantum yield than 366 nm ($\sigma_b \rightarrow \sigma^*$) photolysis as we would expect based on the relative change in M-M bond order in these two cases.

Experimental Section

Materials. The $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ were obtained from Pressure Chemical Co. and were used without further purification. The $\text{Re}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_{10}$ were obtained from Pressure Chemical Co. and were used after sublimation. All solvents used were spectroscopic grade and were used without further purification. The PhCH_2Cl , Ph_3CCl , and CCl_4 were used as commercially available reagent grade chemicals. All analyses were performed by the Alfred Bernhardt Mikroanalytisches Laboratorium.

Spectra. All uv-visible spectra were obtained using a Cary 17 uv-vis-nir spectrophotometer. All ir spectra were recorded using a Perkin-Elmer 521 grating infrared spectrometer. Low temperature uv-visible spectra were obtained in EPA solution with a quartz liquid nitrogen dewar fitted with quartz optical flats for windows. Quantitative ir measurements were made using matched 0.1 mm or 1.0 mm path length NaCl cells obtained from Perkin-Elmer Corp.

$[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$. Both the tungsten and molybdenum dimers were synthesized by the established route¹⁷ beginning with $\text{Mo}(\text{CO})_6$ or $\text{W}(\text{CO})_6$ and sodium cyclopentadienide in THF solution.

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$. An N_2 purged 100-ml CCl_4 solution of 0.2 g (0.41 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ was photolyzed for 1 hr with a GE black lite (two 15-W bulbs with principal output 300–400 nm) or until the ir showed principally the presence of the carbonyl chloride. The solution was rotary evaporated to dryness (35° and 40 mm) and the remaining dimer and the chloride separated by elution from a grade no. 1 alumina column in the dark with CH_2Cl_2 . The chloride came off the column after the dimer and was identified by ir¹⁴ and elemental analysis, yield 0.06 g (40%). The procedure followed for the tungsten chloride was identical and the product was confirmed by ir¹⁴ and elemental analysis, yield 54%.

Synthesis of $(\text{OC})_5\text{M}'\text{-M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ ($\text{M}' = \text{Mn, Re; M} = \text{Mo, W}$). The method of synthesis for all four possible M'-M compounds was the same and can be illustrated by that for the Mn-Mo compound. An N_2 purged 100 ml benzene solution of 0.5 g (1.2 mmol) of $\text{Mn}_2(\text{CO})_{10}$ and 0.6 g (1.23 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ was photolyzed with a 450-W Hanovia medium pressure Hg lamp with a broad band uv filter (300–400 nm) until the ir showed that the rate of product formation had slowed demonstrably (about 1.5–2 hr). Then the solution was evaporated to dryness (35°, 40 mm) and redissolved in a minimum amount of CH_2Cl_2 . The reactants and products were then separated from this solution by chromatography, in the dark, on grade no. 1 alumina. The unreacted $\text{Mn}_2(\text{CO})_{10}$ was eluted with pure isooctane, the $(\text{OC})_5\text{Mn-Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ was then eluted with a 25% solution of CH_2Cl_2 in isooctane, and finally unreacted $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ was eluted with pure CH_2Cl_2 . The product was identified by ir¹⁵ and the yield (0.115 g 85%) was based on $\text{Mn}_2\text{CO}_{10}$ disappearance. Photolysis in the cases where $\text{Re}_2(\text{CO})_{10}$ was used were carried out in Vycor tubes. Synthetic yields based on recovered reactants for the other compounds were Mn-W (70%), Re-Mo (25%), and Re-W (40%). The ir bands (Table II) and the melting points agree with those in the literature:¹⁵ Re-W (mp 109–111°, lit. 110–111.5°), Mn-W (mp 89.5–90°, lit. 90–91°), Mo-Mn (mp 78.5–80.5°, lit. 80.5–81.5°).

Typical Photolysis Procedures. Solutions of the metal carbonyl and a substrate in 3-ml aliquots were placed in Pyrex test tubes (13 × 100 mm) with constrictions. These solutions were degassed in four freeze-pump-thaw cycles and then hermetically sealed. Photolyses were performed with the use of a merry-go-round equipped with either a 450- or a 550-W Hanovia medium pressure Hg source filtered with Corning glass filters and filter solutions to isolate 366-, 436-, or 550-nm mercury emissions. Ferrioxalate actinometry¹⁸ was performed for each experiment to measure the light intensity at 366 and 436 nm. Actinometry with Reinecke's salt¹⁹ was performed to measure light intensity at 550 nm. Analysis of solutions was performed by uv-visible or ir spectroscopic measurements. Quantum yield determinations were repeated at least twice.

Flash Photolysis Experiments. A degassed isooctane solution of ($1 \times 10^{-3} M$) $\text{M}'_2\text{CO}_{10}$ and ($1 \times 10^{-3} M$) $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ in a hermetically sealed Pyrex test tube was flashed zero-five times at 300 J using a Xenon Corp. Model F-710 flash photolysis apparatus as the light source. The samples were subsequently analyzed by ir for the presence of mixed metal products. Molar absorptivities for the M-M' products are included in Table II.

PhCH_2Cl and Ph_3CCl Experiments. Degassed solutions of PhCH_2Cl ($10^{-1} M$) and the metal carbonyl ($2 \times 10^{-3} M$) in 100 ml of isooctane or benzene with octadecane ($5 \times 10^{-3} M$) as an internal standard were photolyzed with a GE black lite or Hanovia Hg lamp. The progress of the reaction was monitored by gas chromatography (Varian series 1400gc with 3% SE-30 column at 200°) for benzyl chloride disappearance and the appearance of bibenzyl and by ir for the disappearance of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ and the appearance of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$. Solutions of Ph_3CCl ($10^{-1} M$) and metal carbonyl ($1 \times 10^{-3} M$) in THF, benzene, or isooctane were degassed in 13 × 100 mm test tubes and a 4 mm o.d. quartz ESR tube. The solutions were irradiated in parallel for 2 min with a GE black lite and the test tubes were analyzed by ir for the metal carbonyl halides, and the ESR tube was analyzed on a Varian E-9 ESR for the presence of the $\text{Ph}_3\text{C}\cdot$ radical.

Acknowledgments. We thank the National Science Foundation for support of this research. Mark S. Wrighton acknowledges support as a Fellow of the A. P. Sloan Foundation, 1974–1976, and David S. Ginley thanks the M.I.T. Chemistry Department for support as a Uniroyal Fellow.

References and Notes

- (1) M. Wrighton and D. Bredesen, *J. Organomet. Chem.*, **50**, C35 (1973).
- (2) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 2065 (1975).
- (3) S. A. Hallock and A. Wojcicki, *J. Organomet. Chem.*, **54**, C27 (1973).
- (4) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **91**, 582 (1969), and references therein.
- (5) M. Wrighton, *Chem. Rev.*, **74**, 401 (1974).
- (6) A. R. Burkett, T. J. Meyer, and D. G. Whitten, *J. Organomet. Chem.*, **67**,

- 67 (1974).
 (7) R. J. Haines, R. S. Nyholm, and M. G. B. Stiddard, *J. Chem. Soc. A*, 43 (1968).
 (8) R. B. King and K. H. Pannell, *Inorg. Chem.*, **7**, 2356 (1968).
 (9) K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967).
 (10) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).
 (11) (a) T. S. Piper and G. Wilkinson, *Naturwissenschaften*, **42**, 625 (1955);
 (b) E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. Anorg. Allg. Chem.*, **282**, 47 (1955).
 (12) R. B. King, *Acc. Chem. Res.*, **3**, 417 (1970).
 (13) G. Wilkinson, *J. Am. Chem. Soc.*, **76**, 209 (1954).
 (14) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).
 (15) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. S. Beschastnov, *Dokl. Akad. Nauk SSSR*, **159**, 377 (1964).
 (16) R. A. Levenson, H. B. Gray, and G. P. Ceasar, *J. Am. Chem. Soc.*, **92**, 3653 (1970).
 (17) R. B. King and F. G. A. Stone, *Inorg. Synth.*, **7**, 107 (1963).
 (18) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
 (19) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).

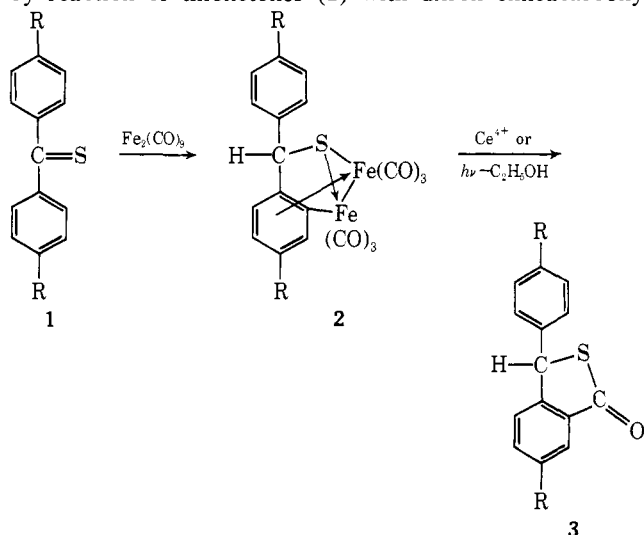
Chemistry of Sulfur-Donor Ligand Ortho-Metalated Iron Carbonyl Complexes and Thiolactones Derived Therefrom

Howard Alper* and William G. Root

Contribution from the Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901. Received October 19, 1974

Abstract: Ortho-metalated iron carbonyl complexes can be converted to isobenzothiophenes (thiolactones), in the presence of *n*-donor ligands such as amines, phosphines, and alcohols. The intermediate in these ligand migration reactions has been isolated. The same transformation can be effected photolytically by use of tetracyanoethylene. Carbonyl insertion and/or desulfurization of the complexes occurred in the presence of anionic reagents (e.g., $^-OC(CH_3)_3$), subject to the nature of the reaction medium. Mercuric acetate cleavage of the complexes results in both ortho-mercuration and desulfurization to give ethers or esters, depending on the reaction conditions. Lactones and/or alkoxy esters resulted when the ortho-metalated complexes were treated with mercuric trifluoroacetate. Lactones were also formed by treatment of the complexes with excess 30% hydrogen peroxide or *m*-chloroperbenzoic acid. Mechanisms are proposed for some of these reactions.

There has been considerable recent interest in the area of transition metal intramolecular ortho-metalation reactions.¹ One of us has reported the first examples of sulfur-donor ligand ortho-metalated complexes (e.g., **2**), formed by reaction of thioketones (**1**) with diiron enneacarbonyl



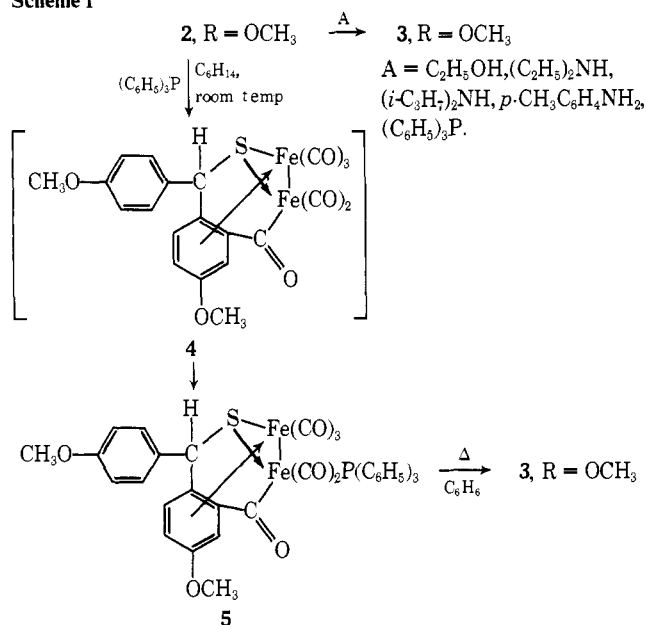
[$Fe_2(CO)_9$]. An initial study of the chemistry of these complexes indicated that they had potential as intermediates for organic synthesis. For instance, oxidative or photolytic cleavage of **2** afforded the relatively little known isobenzothiophene derivatives (**3**) in good yields. This paper describes some new, and synthetically useful, reactions of the ortho-metalated complexes **2**, and of the thiolactones (**3**) derived therefrom.²

Results

(i) ***n*-Donor Induced Carbonyl Insertion.** Treatment of ortho-metalated complexes (e.g., **2**, $R = OCH_3$) with a va-

riety of Lewis bases results in carbonyl insertion to give isobenzothiophene derivatives (e.g., **3**, $R = OCH_3$) in variable yields (Scheme I). Thermolysis of **2**, $R = OCH_3$, in abso-

Scheme I



lute ethanol for 3 days gave the thiolactone **3**, $R = OCH_3$, in 13% yield.¹ Reaction of the complex with diethylamine or diisopropylamine in benzene afforded the thiolactone in 49 and 77% yields, respectively. Treatment of **2**, $R = OCH_3$, with *p*-toluidine gave **3**, $R = OCH_3$, in 18% yield. The isobenzothiophene derivative was isolated in 42% yield by exposure of the complex to triphenylphosphine in hot benzene.

The ortho-metalated complex **2**, $R = OCH_3$, was treated with triphenylphosphine under gentle conditions (hexane,