Photochemistry and Electronic Structure of Bis(dicarbonyl(η^5-cyclopentadienyl)ruthenium) and Its Iron Analogue

Harmon B. Abrahamson, Michael C. Palazzotto, Carol L. Reichel, and Mark S. Wrighton*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received September 5, 1978*

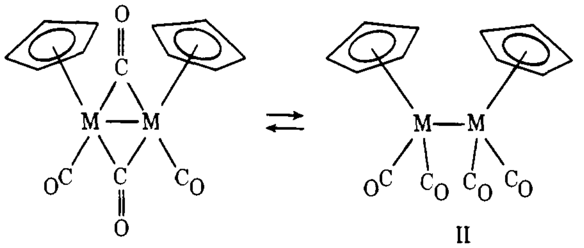
Abstract: The photochemistry and electronic spectra of $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (M = Fe, Ru) are reported. Each complex undergoes efficient M-M bond cleavage subsequent to electronic excitation in CCl_4 solution to yield $[M(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ as the only M-containing product. The disappearance quantum yields at 366 nm for M = Fe and Ru are 0.23 and 0.44, respectively, in CCl_4 where the Fe species is fully in the bridged form and the Ru species is a mixture of the bridged and nonbridged form. The quantum yield for disappearance of the Ru species is the same in CH_3CN and hydrocarbon solution of 0.1 M CCl_4 where the structure in solution is essentially fully bridged (CH_3CN) or ~50/50 bridged/nonbridged (hydrocarbon). The results support the conclusion that carbonyl bridged metal-metal bonds can be efficiently cleaved by optical excitation. The quantum yields for both M = Fe and Ru are somewhat wavelength dependent, with higher energy excitation giving modestly increased quantum yields. The electronic spectrum of the Ru species is very solvent and temperature sensitive in accord with known effects on the equilibrium between the bridged and nonbridged form. The $\sigma_b \rightarrow \sigma^*$ absorption in the bridged form is at ~265 nm and in the nonbridged form it is at ~330 nm, representing a difference of ~7000 cm^{-1} in energy. This result is similar to that reported previously for the bridged and nonbridged forms of $[Co_2(CO)_8]$. $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ is fully bridged under all conditions under consideration here and exhibits a $\sigma_b \rightarrow \sigma^*$ absorption at ~350 nm.

The photochemistry of a number of dinuclear metal-metal bonded organometallic complexes is dominated by cleavage of the metal-metal bond.[1-8] This chemistry is in accord with lowest excited states which involve the population of an orbital which is strongly antibonding (σ^*) with respect to the metal-metal bond.[1,9] All of the complexes for which detailed studies have been reported involve systems for which the metal-metal bond is not bridged. A number of qualitative observations have been described which strongly implicate symmetrical cleavage reactions of bridged systems subsequent to electronic excitation. One good example is represented by the equation[8]

$$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4] \xrightarrow[RX]{h\nu} 2[Fe(\eta^5\text{-}C_5H_5)(CO)_2X] \qquad (1)$$

$$RX = CCl_4, CHCl_3, \text{etc.}$$

$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ is believed to be greater than 99% in the bridged form, **I**, at room temperature, eq 2.[10] However,



I

II

(2)

there are no quantum yield data for the reaction given in eq 1 and such data are necessary in order to assess the reactivity of the lowest electronic excited states of form I. Further, based on the recent report[11] concerning the electronic spectral changes accompanying a temperature-induced shift in the equilibrium distribution of the bridged and nonbridged forms of $[Co_2(CO)_8]$,[12] a significant shift in the equilibrium indicated in eq 2 should result in a large electronic spectral change. In this connection $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ represents an interesting substance, since it is roughly a 1:1 mixture of forms I and II at room temperature in solution[10] but is exclusively bridged in the solid state[13] or at low temperature in solution.[10] Thermodynamic data for equilibrium 2 have been reported previously.[10b]

In this report we describe results concerning the photochemistry and electronic spectroscopy of $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (M = Fe, Ru). Quantum yield data support the conclusion that the complexes are efficiently cleaved to yield mononuclear products when irradiation is carried out in the presence of CCl_4. The spectral studies show a large change in the absorption spectrum of the Ru complex upon lowering the temperature or changing solvent polarity, in accord with shifts in the equilibrium represented in (2). Changes in the spectrum of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ with variation in temperature or solvent polarity are modest by comparison to the Ru analogue, consistent with essentially a fully bridged structure under all conditions.

Results

Electronic and Infrared Absorption Spectra. $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ exhibits a remarkably temperature- and solvent-sensitive absorption spectrum, Figures 1 and 2. As seen in Figure 1, an intense band grows at ~265 nm at the expense of an absorption feature at ~330 nm as the sample is cooled from 298 to 77 K. The large spectral changes are consistent with the equilibrium indicated in (2) where I is the exclusive low-temperature form.[10] Smooth variation in the sample temperature from 298 to 77 K yields substantial spectral changes short of the glassy state of the solvent, and there is fair preservation of an isosbestic point at ~300 nm when solvent contraction is taken into account.

Figures 2 and 3 show comparisons of the UV-vis and IR spectra in isooctane and CH_3CN. EtOH solvent yields a spectrum similar to that obtained in CH_3CN, while CCl_4 solvent yields a spectrum resembling that found in the alkane solvent. Note that the 298 K CH_3CN spectrum is very similar to that in EPA at 77 K; also, the 298 K spectrum in EtOH does not undergo the dramatic change upon cooling the sample to 77 K that is found for EPA solutions. The IR spectrum, Figure 3, is quite different in CH_3CN and isooctane. The differences appear to reflect a change in the ratio of I/II such that more of the bridged species is present in CH_3CN, consistent with the

0002-7863/79/1501-4123$01.00/0

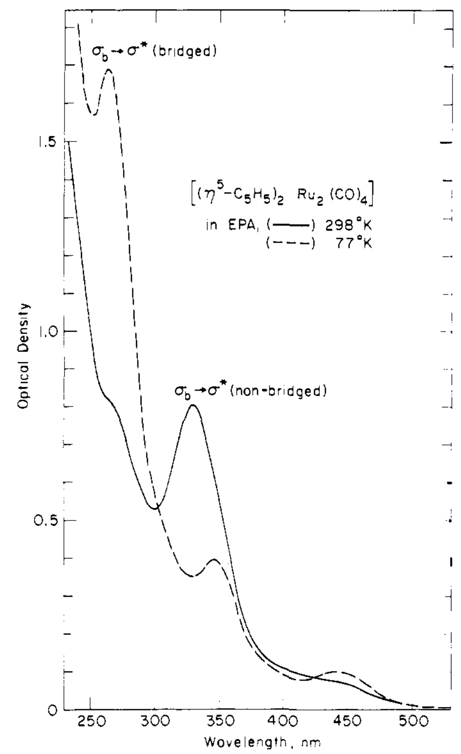


Figure 1. Electronic absorption spectra upon changing the temperature from 298 to 77 K. The spectral changes are not corrected for solvent contraction.

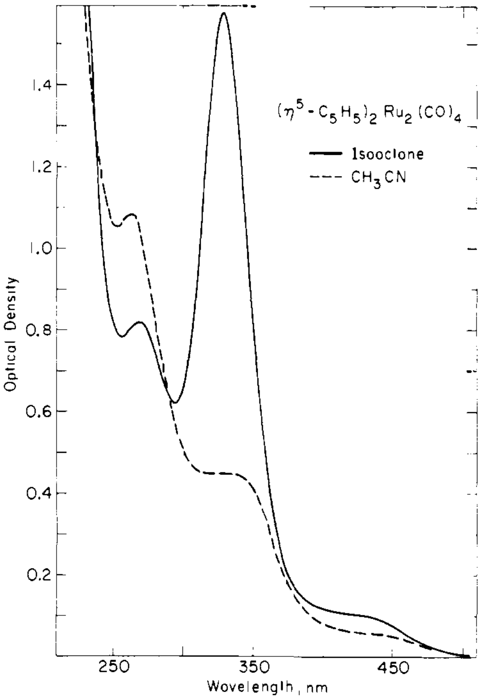


Figure 2. Comparison of electronic absorption spectra of $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in CH_3CN and isooctane at 9.25×10^{-4} M at 298 K in 1.00-cm path cells.

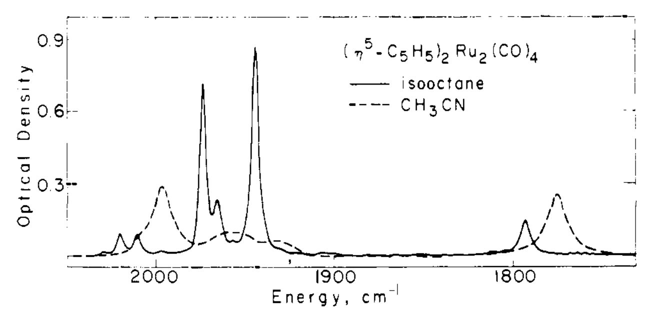


Figure 3. Comparison of infrared spectra in CH_3CN and isooctane at 9.25×10^{-4} M at 298 K in 1.00-mm path cells.

larger integrated area under the 1781-cm^{-1} absorption which has been associated with the bridging carbonyls. Table I lists UV-vis and IR absorptions and associated absorptivities for the Ru species.

By way of contrast to the Ru species, the electronic spectrum of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ is only modestly affected by solvent polarity, Figure 4, or by cooling an EPA solution from 298 to 77 K, Figure 5. In particular, the salient near-UV maximum near 350 nm behaves in a manner quite different than for the band near 330 nm in the analogous Ru complex. UV-vis and IR absorption maxima and molar absorptivities for the Fe complex are included in Table I.

Photochemistry. Irradiation of $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in degassed CCl_4 solution at 298 K results in reaction according to the equation

$$[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4] \xrightarrow[CCl_4]{h\nu} 2[M(\eta^5\text{-}C_5H_5)(CO)_2Cl] \quad (3)$$

$$M = Fe, Ru$$

The reaction can be followed quantitatively by IR using the absorptivities and band positions set out in Table I. For M = Fe there is measurable thermal reaction at 298 K to give the same product, but there is little, if any, detectable reaction for the Ru species on the time scale of the photochemical experiments reported here. Quantum yield data for both complexes are given in Table II.

Irradiation of $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ has also been carried out in dilute solutions of CCl_4 in different solvents. In particular, experiments have been carried out in CH_3CN and in C_6H_6/isooctane (1/24) solutions containing 0.1 M CCl_4. These solvents represent the extremes with respect to the electronic spectral changes observed for the Ru complex, Figure 2. The quantum yield data are included in Table II; the only metal carbonyl product observed is $[Ru(\eta^5\text{-}C_5H_5)(CO)_2Cl]$. Irradiation of $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in the presence of 1-IC_5H_{11} yields only one infrared-detectable product which is assigned as $[Ru(\eta^5\text{-}C_5H_5)(CO)_2I]$; the quantum yield is nearly the same as for reaction with CCl_4.

Irradiation of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in the presence of 0.1 M PPh_3 in degassed benzene solution results in the formation of the monosubstituted dinuclear species:[14]

$$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4] \xrightarrow[0.1\ M\ PPh_3]{h\nu} [Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(PPh_3)] \quad (4)$$

Quantum yield data are included in Table II. Further irradiation of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(PPh_3)]$ in the presence of 0.1 M PPh_3 in methylcyclohexane solution leads to no rapid spectral changes. Irradiation of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in methylcyclohexane solutions of 0.1 M $P(OCH_3)_3$ results in at least two primary products. One of the products is definitely the monosubstitution product, $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(P(OCH_3)_3)]$, based on an infrared spectral comparison with an authentic sample.[14] A second carbonyl product also is a primary product and it is very likely $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(P(OCH_3)_3)_2]$ with bands at 2014 and 1716 cm^{-1}; the same product bands are obtained by irradiating $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(P(OCH_3)_3)]$ in the presence of $P(OCH_3)_3$. Multiple substitution products were noted previously[14] but were not characterized. The important finding here is that the bands

Table I. Spectral Properties of Relevant Complexes[a]

complex	IR, cm^{-1} (ϵ)	UV-vis, nm (ϵ)
[$Ru_2(\eta^5$-$C_5H_5)_2(CO)_4$]	2026 (180), 2016 (530), 2009 (1150), 1971 (4320), 1963 (1880), 1939 (4150), 1781 (1262)	435 (1280), 330 (13 900), 265 (10 950)
[$Ru(\eta^5$-$C_5H_5)(CO)_2Cl$]	2057 (3030), 2009 (3210)	285 (2480)
[$Ru(\eta^5$-$C_5H_5)(CO)_2I$]	2050 (---), 2003 (---)	
[$Fe_2(\eta$-$C_5H_5)_2(CO)_4$]	2004 (2630), 1958 (3450), 1783 (3160), 1996 (2770),[b] 1952 (2440),[b] 1780 (4130)[b]	514 (710),[b] 410 (1870),[b] 346 (9190)[b]
[$Fe_2(\eta^5$-$C_5H_5)_2(CO)_3(P(OCH_3))$]	1965,[c] 1945,[c] 1752[c]	565,[c] 415,[c] 353[c]
[$Fe_2(\eta^5$-$C_5H_5)_2(CO)_2(P(OCH_3))_2$]	2014,[c] 1716[c]	
[$Fe(\eta^5$-$C_5H_5)_2(CO)_2Cl$]	2054 (3290), 2011 (3080), 2049 (2270),[b] 2003 (2340)[b]	403 (590), 339 (880)
[$Fe_2(\eta^5$-$C_5H_5)_2(CO)_3(PPh_3)$]	1961 (1870),[c] 1937 (1507),[c] 1740 (3700),[c] 1950 (1440),[b] 1930 (940),[b] 1732 (4870)[b]	615,[c] 430,[c] 360[c]
[$Fe(\eta^5$-$C_5H_5)(CO)_2I$]	2037 (2370),[b] 1993 (2490)[b]	

[a] All spectral data are for CCl_4 solutions at 298 K unless noted otherwise. [b] Benzene solution at 298 K. [c] Methylcyclohexane solution at 298 K.

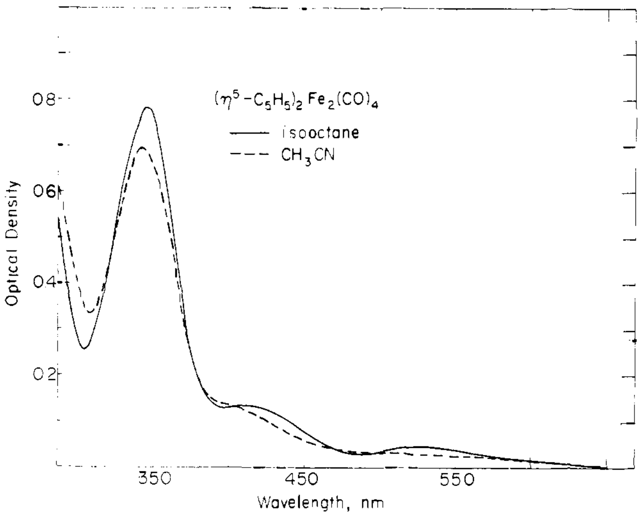


Figure 4. Comparison of electronic spectrum of [$Fe_2(\eta^5$-$C_5H_5)_2(CO)_4$] in isooctane and CH_3CN. Concentration of the complex is 8.3×10^{-5} M in each case and a 1.00-cm path cell was used.

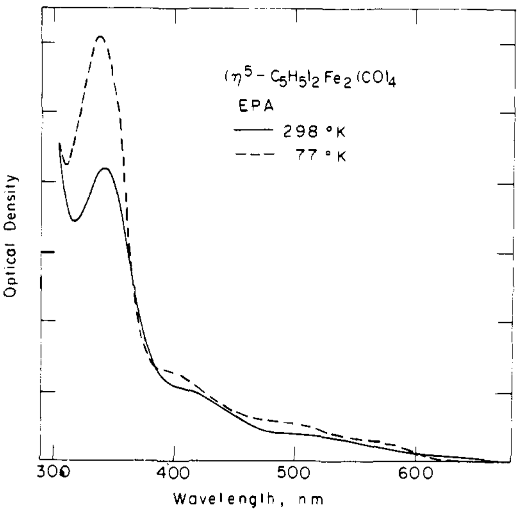


Figure 5. Spectral changes upon lowering the temperature from 298 to 77 K. Changes are not corrected for solvent contraction.

at 1752 and 1716 cm^{-1} grow in together and the formation of the multiple substitution does not require irradiation of the monosubstituted species.

Irradiation of [$Fe_2(\eta^5$-$C_5H_5)_2(CO)_4$] in degassed benzene solution containing 0.1 M PPh_3 and 0.1 M CCl_4 yields no IR-detectable [$Fe_2(\eta^5$-$C_5H_5)_2(CO)_3(PPh_3)$]. The dominant product under these conditions is [$Fe(\eta^5$-$C_5H_5)(CO)_2Cl$]. Figure 6 shows the results found for suppression of the formation of [$Fe_2(\eta^5$-$C_5H_5)_2(CO)_3(PPh_3)$] by using 0.1 M 1-IC_5H_{11} instead of 0.1 M CCl_4. In this case the major product is still [$Fe_2(\eta^5$-$C_5H_5)_2(CO)_3(PPh_3)$], but [$Fe(\eta^5$-$C_5H_5)$-$(CO)_2I$] is formed to the small extent that formation of [$Fe_2(\eta^5$-$C_5H_5)_2(CO)_3(PPh_3)$] is suppressed.

Discussion

The photochemistry found here appears to parallel that found for all other dinuclear metal-metal bonded carbonyl complexes.[1-7] However, what is remarkable here is the fact that the [$M_2(\eta^5$-$C_5H_5)_2(CO)_4$] species have bridging COs to a greater or lesser extent depending on M.[10] Further, the large spectral changes for M = Ru with variation in solvent or temperature are in accord with the notion that the equilibrium ratio of the nonbridged to the bridged form decreases at lower temperature[10] and apparently with more polar solvents as well. We assign the intense near-UV absorption feature at ~330 nm in the Ru complex at 298 K to the $\sigma_b \rightarrow \sigma^*$ excitation of the nonbridged form. Such a spectral feature has come to be regarded[9] as a characteristic of M-M bonded complexes; the mononuclear [$Ru(\eta^5$-$C_5H_5)CO_2X$] species have no such low-energy intense absorption. Upon cooling the solution to 77 K the 330-nm feature significantly diminishes and growth of the absorption at ~265 nm is substantial. We assign the 265-nm feature to a $\sigma_b \rightarrow \sigma^*$ excitation of the CO bridged Ru species. Likewise, the relative absorption (UV-vis and IR) spectra in isooctane (~50/50 bridged/nonbridged)[10] and CH_3CN (apparently fully bridged) are in accord with this assignment. Consistently, the Fe complex does not exhibit substantial temperature or solvent effects, since it is ~99% bridged in solution at 298 K in alkane solvent.[10] We adopt the earlier assignment that the absorption feature at ~350 nm is due to the $\sigma_b \rightarrow \sigma^*$ of the bridged Fe species.[9c] We previously argued[1a] that the $\sigma_b \rightarrow \sigma^*$ position of the nonbridged Fe species would be in the vicinity of ~420 nm and the differences in the spectrum in isooctane and CH_3CN in that region may in fact be due to the small amount of nonbridged material present in alkane solvent which is not present in the more polar CH_3CN.

The $\sigma_b \rightarrow \sigma^*$ positions for the bridged and nonbridged forms of the Ru species differ by ~7000 cm^{-1}. This difference is very similar to that found in the [$Co_2(CO)_8$] system[11] where an equilibrium as in (2) also obtains.[12] The higher energy $\sigma_b \rightarrow \sigma^*$ absorption in the bridged species is possibly a consequence of a shorter metal-metal bond distance. Also, it should be indicated that the assignment of the absorption band as $\sigma_b \rightarrow \sigma^*$ for the bridged form is made with the understanding that the bridging COs seriously alter the orbital scheme. But the ap-

Table II. Reaction Quantum Yields for $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$

M	conditions[a]	product	Φ_{dis}[b]			Φ_{appear}[b]		
			313	366	436	313	366	436
Ru	neat CCl_4	$[Ru(\eta^5\text{-}C_5H_5)(CO)_2Cl]$		0.44			0.92	
	0.1 M CCl_4 in C_6H_6/isooctane (1/24)	$[Ru(\eta^5\text{-}C_5H_5)(CO)_2Cl]$	0.46	0.35	0.36			
	0.1 M CCl_4 in CH_3CN	$[Ru(\eta^5\text{-}C_5H_5)(CO)_2Cl]$	0.55	0.37	0.28			
	0.1 M 1-IC_5H_{11} in C_6H_6/isooctane (1/24)	$[Ru(\eta^5\text{-}C_5H_5)(CO)_2I]$		0.45				
Fe	neat CCl_4	$[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]$	0.38	0.23	0.21	1.06	0.42	0.54
	0.1 M PPh_3 in benzene	$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3PPh_3]$		0.05			0.06	

[a] Degassed solutions of starting complex (~10^{-3} M) irradiated at 366 nm in hermetically sealed ampules. [b] Quantum yields for disappearance (Φ_{dis}) of starting complex and appearance (Φ_{appear}) of product; error is ±10%.

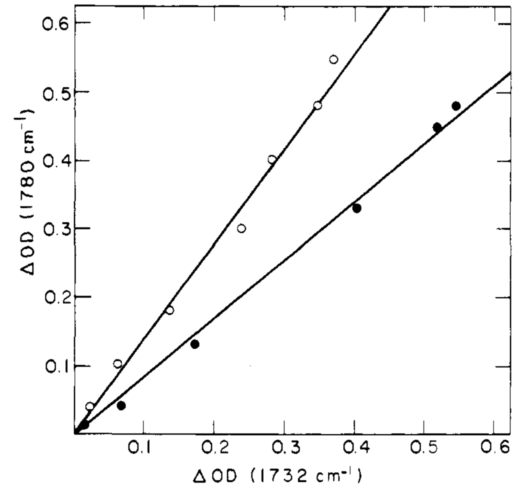


Figure 6. Plot of IR absorption due to $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (1780 cm^{-1}, ϵ 4130) and $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(PPh_3)_2$ (1732 cm^{-1}, ϵ 4870) upon irradiation of 0.03 M $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in deoxygenated benzene solution in the presence of 0.1 M PPh_3 (●) or 0.1 M PPh_3 plus 0.1 M 1-IC_5H_{11} (○). Absorptions were measured in a 0.1-mm path cell.

pearance of the spectral feature (solvent and temperature dependence) is consistent with the $\sigma_b \rightarrow \sigma^*$ type assignment. The weaker shoulders and lower energy maxima for the metal-metal bonded species are attributable to π-d$\rightarrow\sigma^*$ transitions but cannot be assigned in detail.

The photochemistry of $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ is consistent with electronic transitions which terminate in a σ^* orbital with respect to the M-M bond. We have previously reported the synthesis of heterodinuclear metal-metal bonded complexes by simultaneous irradiation of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ and a second homodinuclear metal-metal bonded complex.[1a] The equation

$$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6] + [Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4] \xrightarrow{h\nu} 2[(OC)_2(\eta^5\text{-}C_5H_5)Fe\text{-}Mo(\eta^5\text{-}C_5H_5)(CO)_3] \quad (5)$$

is representative of the chemistry; such is consistent with the photogeneration of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ radicals from $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$. In the presence of CCl_4 the metal-centered radicals abstract Cl to form $[Fe(\eta^5\text{-}C_5H_5)_2(CO)_2Cl]$. Photogeneration of P-donor substitution products likely occurs via substitution of CO by the P donor at the radical stage rather than by dissociative loss of CO from the excited $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$. This interpretation is supported by the observation that the presence of halocarbons can quench the formation of the simple substitution products. Neither CCl_4 nor 1-IC_5H_{11} should be competitive with an equal concentration of PPh_3 for coordinatively unsaturated $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3]$. The lower retardation of the substitution by 1-IC_5H_{11} vs. CCl_4 is in accord with the lower reactivity of 1-IC_5H_{11}.[1a] Further, the observation of a multiple substitution product as a *primary* photoproduct from the photolysis of the Fe species in the presence of $P(OCH_3)_3$ is inconsistent with the dissociative loss of CO as the primary photoprocess, whereas such a product could result from the coupling of two substituted radicals.[15] The substitution lability of 17e$^-$ metal-centered radicals is well established.[7]

The reaction quantum yields are only modestly affected by variation in the excitation wavelength which suggests that the upper excited states are more reactive than the lowest excited states. This trend is consistent with the fact that the lowest excited states are d$\pi \rightarrow \sigma^*$ type and the M-M bond order is not as diminished as in the $\sigma_b \rightarrow \sigma^*$ excited states populated at the higher energies. Such wavelength effects on M-M bond cleavage have been noted previously.[1c]

The quantum efficiency for the Fe-Fe bond homolysis is quite high despite the fact that the species is principally CO bridged under the conditions of the irradiation. Irradiation of the Ru complex provides further evidence for the efficient scission of a bridged metal-metal bond. The reaction quantum yields in CH_3CN vs. the hydrocarbon solvent are essentially the same, despite the fact that the equilibrium indicated in (2) is substantially altered. In fact, the differences in quantum yield are not outside what could be interpreted as just a "solvent effect". The bridged complexes have reaction quantum yields which are similar to those for nonbridged complexes.[1] Unfortunately, quantum yield data do not provide absolute rate constants for reaction, and it is consequently impossible to make a detailed comparison of excited-state reactivities of bridged and nonbridged complexes. It would be of interest, too, to learn the position of equilibrium 2 in the excited state. Since the $\sigma_b \rightarrow \sigma^*$ for the nonbridged is at lower energy, excitation of the bridged species may yield an excited, nonbridged complex which either nonradiatively decays to the ground state or fragments to two radicals.

Experimental Section

Materials. All solvents for photochemical and spectroscopic studies were used as received in commercially available spectroquality. $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ was used as obtained from commerical sources after recrystallization from hexane/CH_2Cl_2. Its spectral properties are consistent with those previously reported. $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ was prepared according to the published literature procedure.[16] Commercially available $[RuCl_3 \cdot nH_2O]$ was converted to $[RuI_3]$ by dissolving 7.3 g of $[RuCl_3 \cdot nH_2O]$ in a minimum amount of H_2O and mixing with ~40 mL of saturated aqueous KI. The solution was heated gently while stirring and black crystals formed. The crystals were collected by filtration and washed with dilute KI solution and then with absolute EtOH. The resulting RuI_3 was placed in a vacuum desiccator overnight to remove any residual H_2O. Conversion of $[RuI_3]$ to $[Ru(CO)_2I_2]_n$ was effected by heating solid $[RuI_3]$ in a boat in a tube furnace at 220 °C while CO was passed through the tube. The reaction continued until the color of the solid changed from black ($[RuI_3]$) to orange-red ($[Ru(CO)_2I_2]_n$). The $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ was finally obtained from reaction of $Na[C_5H_5]\cdot$DME with $[Ru(CO)_2I_2]_n$. $[Ru(CO)_2I_2]_n$ (10.9 g) and 10 g of $Na[C_5H_5]\cdot$DME were dissolved in 100 mL of DME and refluxed for ~15 h, after which time the solution had turned very dark and IR indicated the presence of absorptions attributable to [$Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4$]. The solution was filtered and the solvent was removed under vacuum. The solid was taken up in benzene, leaving a large amount of an insoluble dark solid. The benzene solution contained the desired product and [$Ru(\eta^5\text{-}C_5H_5)_2$]. The mixture was chromatographed on alumina with [$Ru(\eta^5\text{-}C_5H_5)_2$] eluting first with benzene followed by [$Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4$]. The benzene was removed under vacuum. Final purification was by chromatography on alumina under Ar eluting with benzene. The final material was handled under inert atmosphere and the golden-orange solid was stored in a Schlenk tube under Ar. An elemental analysis of the [$Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4$] was satisfactory (Alfred Bernhardt, West Germany). Anal. Calcd for $C_{14}H_{10}O_4Ru_2$: C, 37.84; H, 2.27; O, 14.40. Found: C, 38.04; H, 2.26; O, 14.62. Spectral properties are in accord with those previously reported.[10,16]

An authentic sample of [$Ru(\eta^5\text{-}C_5H_5)(CO)_2Cl$] was prepared by irradiation of [$Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4$] in CCl_4. [$Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4$] (0.2 g) was dissolved in 125 mL of CCl_4 and placed in an Erlenmeyer flask. The solution was purged continuously with prepurified N_2 and irradiated with a G.E. Blacklite equipped with two 15-W bulbs with principal output in the near-UV centered at 355 nm. The photoreaction was followed by IR until ~90% consumption of starting material obtained (~2 h). The solution showed IR absorptions at 2055 and 2004 cm^{-1} corresponding to [$Ru(\eta^5\text{-}C_5H_5)(CO)_2Cl$]. The solution was rotary evaporated to dryness and the residue was chromatographed on alumina eluting with CH_2Cl_2. By IR, the first compound eluted was [$Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4$] and the desired compound eluted second. Solvent (CH_2Cl_2) was removed by rotary evaporation. An elemental analysis for [$Ru(\eta^5\text{-}C_5H_5)(CO)_2Cl$] was satisfactory (Alfred Bernhardt, West Germany). Anal. Calcd for $C_7H_5O_2ClRu$: C, 32.63; H, 1.96; Cl, 13.76; O, 12.42. Found: C, 32.51; H, 2.09; Cl, 13.81; O, 12.58. The [$Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl$] sample was that used in earlier studies.[1a] Samples of the P-donor substituted Fe dimers were prepared according to the literature procedure and IR spectral data were consistent with the previous report.[14]

Spectra. All IR spectra were recorded using a Perkin-Elmer 180 spectrometer using matched 0.1- or 1.0-mm path NaCl or KBr cells. Electronic absorption spectra were recorded using a Cary 17 UV-vis-near-IR spectrophotometer. Low-temperature spectra were recorded using an all-quartz liquid N_2 Dewar with optical quality flats for windows.

Photochemistry. Photochemical experiments were carried out using either a G.E. Blacklite (355 nm) or an appropriately filtered (313, 366, or 436 nm) 450- or 550-W Hanovia medium-pressure Hg lamp with a merry-go-round.[1] The light intensity was determined by ferrioxalate actinometry[18] and was in the range of 1.85×10^{-6} to 5×10^{-9} einstein/min. Samples for quantum yield determinations were freeze-pump-thaw degassed, hermetically sealed samples in 13-mm o.d. Pyrex ampules. Concentration of [$M_2(\eta^5\text{-}C_5H_5)_2(CO)_4$] was in the range 10^{-4} to 2×10^{-3} M to ensure ~100% light absorption and quantum yields are for conversions of <20%.

Acknowledgments. We thank the National Science Foundation and the Office of Naval Research for support of this research. H.B.A. acknowledges support as an NSF Predoctoral Fellow, 1975-1978, and M.S.W. as a Dreyfus Teacher-Scholar Grant recipient, 1975-1980. We thank Professor Harry B. Gray of the California Institute of Technology for a preprint of the work described in ref 15.

References and Notes

(1) (a) H. B. Abrahamson and M. S. Wrighton, *Inorg. Chem.*, **17**, 1003 (1978); *J. Am. Chem. Soc.*, **99**, 5510 (1977); (b) M. Wrighton and D. Bredesen, *J. Organomet. Chem.*, **50**, C35 (1973); (c) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 2065, 4246, 4908 (1975); (d) D. L. Morse and M. S. Wrighton, *ibid.*, **98**, 3931 (1976).

(2) (a) J. L. Hughey, IV, C. R. Bock, and T. J. Meyer, *J. Am. Chem. Soc.*, **97**, 4440 (1975); (b) J. L. Hughey, IV, C. P. Anderson, and T. J. Meyer, *J. Organomet. Chem.*, **125**, C49 (1977).

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

(4) R. M. Laine and P. C. Ford, *Inorg. Chem.*, **16**, 388 (1977).

(5) (a) A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 966 (1974); (b) A. Hudson, M. F. Lappert, and B. K. Nicholson, *J. Chem. Soc., Dalton Trans.*, 551 (1977).

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

(7) (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).

(8) C. Giannotti and G. Merle, *J. Organomet. Chem.*, **105**, 97 (1976).

(9) (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); *Inorg. Chem.*, **14**, 1215 (1975).

(10) (a) R. D. Fischer, A. Vogler, and K. Noack, *J. Organomet. Chem.*, **7**, 135 (1967); (b) K. Noack, *ibid.*, **7**, 151 (1967); (c) P. McArdle and A. R. Manning, *J. Chem. Soc. A*, 2128 (1970).

(11) 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).

(12) (a) A. Noack, *Helv. Chim. Acta*, **47**, 1064 (1964); (b) G. Bor and K. Noack, *J. Organomet. Chem.*, **64**, 367 (1974); (c) G. Bor, U. K. Dietler, and K. Noack, *J. Chem. Soc., Chem. Commun.*, 914 (1976); (d) S. Onaka and D. F. Shriver, *Inorg. Chem.*, **15**, 915 (1976); (e) R. L. Sweany and T. L. Brown, *ibid.*, **16**, 415 (1977).

(13) O. S. Mills and J. P. Nice, *J. Organomet. Chem.*, **9**, 339 (1967).

(14) R. J. Haines and A. L. duPreez, *Inorg. Chem.*, **8**, 1459 (1969).

(15) In contrast to results for $P(OCH_3)_3$, the irradiation of [$Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4$] in the presence of $P(O\text{-}i\text{-}Pr)_3$ yields only monosubstitution and evidence has been obtained for an intermediate dinuclear iron complex which is CO bridged but not Fe–Fe bonded: D. R. Tyler, M. A. Schmidt, and H. B. Gray, *J. Am. Chem. Soc.*, **101**, 2753 (1979).

(16) E. O. Fischer and A. Vogler, *Z. Naturforsch. B*, *17*, 421 (1962).

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

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