models to date of the expected changes in heme geometry for hemoproteins undergoing thermal spin equilibria. The question of whether the increased size of the high-spin iron(III) atom in the mixed-ligand derivatives will be accommodated by similar magnitudes of iron atom displacement and porphinato core expansion as observed in Fe(OEP)(py)(NCS) is a question being actively pursued.

Acknowledgment. We thank the National Institutes of Health for support of this work (at Notre Dame) under Grant HL-15627. We are grateful to Professors P. G. Rasmussen and Larry Garber for access to magnetic susceptibility apparatus. We thank Setsuko Kato for assistance with the NMR measurements.

Registry No. Fe(TPP)(py)(NCS)·$^1/_2$py, 81602-85-9; Fe(OEP)(py)(NCS), 81602-86-0.

Supplementary Material Available: Table III, anisotropic thermal parameters for Fe(TPP)(py)(NCS), Table V, anisotropic thermal parameters for Fe(OEP)(py)(NCS), and listings of observed and calculated structure amplitudes (×10) for Fe(TPP)(py)(NCS) and Fe(OEP)(py)(NCS) (51 pages). Ordering information is given on any current masthead page.

Adduct-Mediated Photochemistry. Evidence for Excited-State Reordering in (Acetophenone)tricarbonylchromium(0) upon Adduct Formation with Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium(III)

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Abstract: The electronic spectra of several (arene)tricarbonylchromium(0) complexes (arene = aniline, anisole, benzaldehyde, benzene, acetophenone, acenaphthene) and the photochemical reactivity of the latter three species have been investigated in isooctane solution in the absence and presence of the title europium(III) β-diketonate complex, Eu(fod)$_3$. These complexes possess a band whose positional dependence on arene substituent leads to its assignment as predominantly Cr → arene charge transfer (MLCT). Addition of Eu(fod)$_3$ produced spectroscopic changes only for the acetophenone and benzaldehyde complexes, red-shifting the λ_{max} values of their MLCT bands by over 1000 cm^{-1} and shifting their IR terminal carbonyl stretching bands to higher energy by ~10 cm^{-1}. These spectral changes are ascribed to adduct formation wherein the arene carbonyl oxygen atom, serving as a site of Lewis basicity, coordinates to the Lewis acid, Eu(fod)$_3$. Spectrophotometric titrations support the presence of predominantly 1:1 adducts whose formation constants are ~10^3 M^{-1}. Visible and near-UV photolysis of the benzene, acetophenone, and acenaphthene complexes in 1-pentene/isooctane solution results in the disappearance of the complexes, presumably through photosubstitution of CO by 1-pentene, with quantum efficiencies, ϕ_d, of ~0.7, 0.2, and 0.001, respectively. Addition of Eu(fod)$_3$ affected ϕ_d for only the acetophenone complex: spectroscopic evidence indicates that the adduct undergoes the same photoreaction as the free complex but far less efficiently—ϕ_d is ~0.02. The decline in ϕ_d for the complexes examined roughly parallels the red-shift in their MLCT bands and is consistent with a model developed for other low-spin d^6 systems: the MLCT excited state is believed to be inert toward substitution; as it is tuned to below a ligand field excited state whose population leads to substitution, ϕ_d diminishes. The adduct photoreactivity is readily subsumed in this excited-state reordering model. Implications of adduct-mediated perturbation of excited-state properties are discussed.

Photochemists have recognized for some time that environment can profoundly affect molecular excited-state processes. Among the more well-studied sources of environmental perturbation are solvent, temperature, and heavy-atom effects.[1] Another technique for altering the molecular milieu is adduct formation. Although the excited-state properties of a number of complexes derived from organic constituents have been examined,[2] there are few such studies where one or both of the precursors is an organometallic species. A notable exception involves studies of the effect of adduct formation on the emissive properties of lanthanide β-diketonate complexes.[3] That adducts can be formed from a wide range of organometallic species has, of course, been amply demonstrated.[4]

Scheme I

$$\mathrm{A} \xrightarrow{h\nu} \mathrm{B} \tag{1}$$

$$\mathrm{A} + \mathrm{M} \rightleftharpoons \mathrm{AM} \tag{2}$$

$$\mathrm{AM} \xrightarrow{h\nu} \text{no reaction} \tag{3}$$

$$\mathrm{AM} \xrightarrow{h\nu} \mathrm{CM} \rightleftharpoons \mathrm{C} + \mathrm{M} \xrightarrow{-\mathrm{M}} \mathrm{C} \tag{4}$$

$$\mathrm{AM} \xrightarrow{h\nu} \mathrm{BM} \rightleftharpoons \mathrm{B} + \mathrm{M} \xrightarrow{-\mathrm{M}} \mathrm{B} \tag{5}$$

In searching for systems where the effects of adduct formation on photoreactions might be explored, we had the reactions of Scheme I in mind as possibilities. Ideally, we sought a photoreactive species, A, which would complex with a photoinert species, M, in a Lewis acid–base equilibrium, eq 2. If the adduct were

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[1] Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, Calif., 1978; e.g., Chapters 5, 6, and 8.

[2] Davidson, R. S. In "Molecular Association"; Foster, R.; Ed.; Academic Press: New York, 1975; Vol. I, Chapter 4, and references therein.

[3] See, for example: (a) Brittain, H. G. *Inorg. Chem.* **1980**, *19*, 640. (b) *J. Chem. Soc., Dalton Trans.* **1979**, 1187. (c) Brittain, H. G.; Richardson, F. S. *J. Am. Chem. Soc.* **1976**, *98*, 5858. (d) *J. Chem. Soc., Dalton Trans.* **1976**, 2253.

[4] See, for example: (a) Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231. (b) Marks, T. J.; Porter, R.; Kristoff, J. S.; Shriver, D. F. In "Nuclear Magnetic Resonance Shift Reagents"; Sievers, R. E.; Ed.; Academic Press: New York, 1973; p 247. (c) Drago, R. S. *Coord. Chem. Rev.* **1980**, *33*, 251. (d) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093.

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photolyzed, preferably in a spectral region where little or no absorption by A or M occurs, we envisioned eq 3, 4, and 5 as possible consequences. In eq 3 the adduct serves to completely quench the normal photoreaction of A to produce B (eq 1). Adduct formation thereby renders an otherwise photoreactive species photoinert and would be useful for protecting such systems from light.

The possibility of altering the photoproducts of A by adduct formation is embodied in eq 4: photolysis of AM produces CM, yielding, upon removal of M from the system, the species C. We have recently demonstrated the viability of this pathway in studies of adducts formed from retinal isomers and tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium(III), Eu(fod)$_3$.[5] In this system efficient light absorption occurred at photon energies lower than those absorbed by the uncomplexed retinal isomers; additionally, the isomeric composition of the photolysate differed substantially from that obtained in the absence of Eu(fod)$_3$. Results of this nature may be synthetically useful.

A third scenario is given by eq 5 in which the photoproduct is BM. Upon removal of M, the same product, B, is obtained as in the photolysis of uncomplexed A. Although the net reaction is the same, eq 1 and 5 could differ, e.g., in quantum efficiency. This situation is illustrated by the adduct discussed in this paper, an adduct having as constituents Eu(fod)$_3$ and (acetophenone)tricarbonylchromium(0), (AcPh)Cr(CO)$_3$.

Our selection of Eu(fod)$_3$ as the Lewis acid partner in the adduct is based on several features we found desirable in our studies of retinal•Eu(fod)$_3$ adducts. Besides being commercially available, Eu(fod)$_3$ is highly soluble in nonpolar solvents; it coordinates readily to many Lewis bases with N- or O-donor atoms; and the complex absorbs very little of the visible spectrum, although it does possess an intense intraligand band ($\lambda_{max} \approx 290$ nm ($\epsilon \sim 30\,000$ M^{-1} cm^{-1})). Of course, the solubility and coordinative unsaturation of Eu(fod)$_3$ account for its popularity as an NMR shift reagent.[6]

In choosing a photoactive organometallic Lewis base, we sought systems where some understanding of the factors controlling variable photoreactivity was available. Particularly attractive compounds are low-spin d^6 systems possessing metal-to-ligand charge-transfer (MLCT) excited states in addition to ligand field (LF) excited states. Studies of $Ru(NH_3)_5L^{2+}$,[7] $W(CO)_5L$,[8] *cis*-$W(CO)_4L_2$,[9] $CpM(CO)_2L$ (Cp = η^5-C_5H_5; M = Mn, Re),[10] and $Fe(CN)_5L^{3-}$[11] (L = pyridine or a substituted pyridine) demonstrated that the efficiency of photosubstitution could often be varied over several orders of magnitude by varying the substituent of the pyridine ligand. The explanation which has emerged from these studies has to do with the relative energies of the LF and MLCT excited states: when the LF state is lowest in energy, efficient photosubstitution obtains; as the MLCT state is tuned to below the LF state by varying the pyridyl substituent, the photoreaction is shut off.

In this study we examine the photoreactivity of low-spin d^6 (arene)tricarbonylchromium(0) complexes. In particular, we provide spectroscopic evidence for adduct formation between (AcPh)Cr(CO)$_3$ and Eu(fod)$_3$ and demonstrate that adduct formation perturbs the photoreactivity of (AcPh)Cr(CO)$_3$ in a manner consistent with the reordering of LF and MLCT excited states. The insight obtained from this study can be used to explain effects observed in other adduct systems and suggests strategies for the design of specific adduct-mediated excited-state processes.

Results and Discussion

The interaction of Eu(fod)$_3$ with several (arene)tricarbonylchromium(0), ATCr, species in addition to (AcPh)Cr(CO)$_3$ was examined. Sections below describe the electronic and infrared spectra of these mixtures as well as their photochemistry. The final section discusses the mechanistic implications of the adduct-mediated photoreactions.

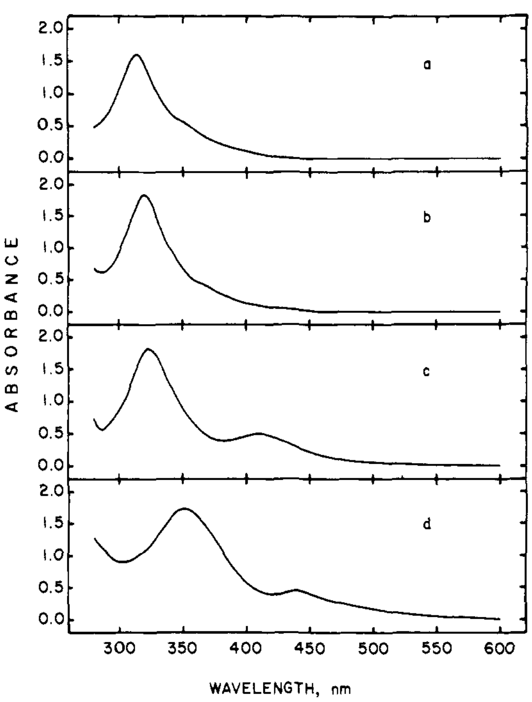


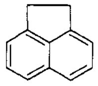
Figure 1. Electronic spectra at 295 K in isooctane of several ATCr complexes: A = 0.16 mM (anisole)Cr(CO)$_3$; B = 0.17 mM (benzene)Cr(CO)$_3$; C = 0.18 mM (acetophenone)Cr(CO)$_3$; D = 0.21 mM (acenaphthene)Cr(CO)$_3$. Cell path length is 1.0 cm.

Table I. Electronic Absorption Spectral Features for (Arene)Cr(CO)$_3$ Complexes and Adducts[a]

arene	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
aniline, $C_6H_5NH_2$	350 (3550),[d] 320 (9330)
anisole, $C_6H_5OCH_3$	350 (3600),[d] 317 (10 300)
benzene, C_6H_6	375 (3000),[d] 320 (10 600)
acetophenone, $C_6H_5C(O)CH_3$	409 (2450), 327 (10 400)
benzaldehyde, C_6H_5CHO	415 (2540), 322 (9330)
acenaphthene[b]	437 (1880), 352 (8130)
acetophenone adduct[c]	448 (3920)
benzaldehyde adduct[c]	435 (3430)

[a] Spectra recorded in N_2-saturated isooctane solution at 295 K.

[b] Acenaphthene is



[c] Spectral data given are for solutions to which further addition of Eu(fod)$_3$ produced little change in the spectra; i.e., limiting spectra. Absorptivities are calculated on the basis of the starting ATCr complex concentration and assume a 1:1 adduct. [d] Inflection point.

Electronic Spectra. We have examined the electronic spectra of several ATCr complexes in hydrocarbon solvents. Their principal features are illustrated in Figure 1 and summarized in Table I. With the exception of the acenaphthene complex, all of the ATCr complexes possess an intense ($\epsilon \sim 10^4$ M^{-1} cm^{-1}) band at ~315–330 nm and a slightly weaker band whose position varies from ~350 to 415 nm, depending on the arene substituent. The assignment of the higher energy band does not appear well established in the literature,[12] although its intensity and relative independence of arene substituent suggest that a predominantly Cr $\rightarrow \pi^*$ CO CT assignment may be appropriate. However, we will be most concerned with the lower energy band whose positional dependence on the arene substituent is consistent with a Cr $\rightarrow$ arene CT assignment. In particular, Table I shows that

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[5] Ellis, A. B.; Schreiner, R.; Ulkus, R. A. *Proc. Natl. Acad. Sci., U.S.A.* **1981**, *78*, 3993.

[6] Rondeau, R. E.; Sievers, R. E. *J. Am. Chem. Soc.* **1971**, *93*, 1522.

[7] (a) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 601. (b) *Ibid.* **1977**, *99*, 7213.

[8] Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105.

[9] Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* **1978**, *17*, 3385.

[10] Giordano, P. J.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 160.

[11] Figard, J. E.; Petersen, J. D. *Inorg. Chem.* **1978**, *17*, 1059.

[12] Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979; p 59.

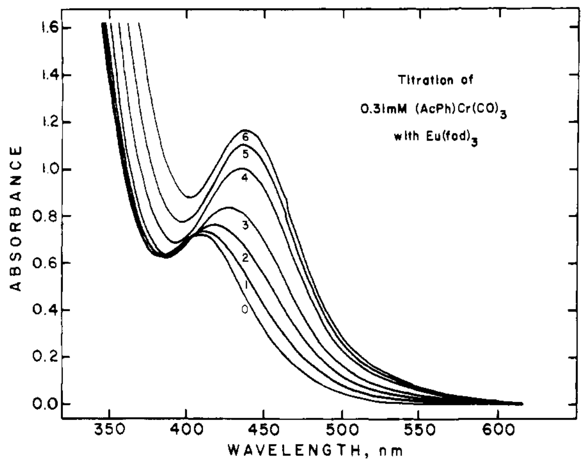

Figure 2. Electronic spectral changes (295 K) accompanying the addition of a 0.17 M $Eu(fod)_3$ isooctane solution to an $(AcPh)Cr(CO)_3$ isooctane solution in a 1.0-cm path length cell. Curves 0 through 6 represent 0, 0.22, 0.66, 1.5, 3.9, 7.2, and 11 equiv of $Eu(fod)_3$, respectively. The "bump" at 464 nm in the last three spectra is a Eu(III) f-f band.

the band smoothly red-shifts as the substituent is changed from the electron-donating NH_2 and OCH_3 groups to the electron-withdrawing CHO and $C(O)CH_3$ groups. Although LF transitions may also contribute to the observed band intensities, they are typically weaker and should be relatively unaffected by arene substituents, since the donor atoms directly coordinated to the metal are unchanged throughout the arene series.

Further support for the Cr → arene CT assignment comes from studies of the interaction of $Eu(fod)_3$ with ATCr complexes in isooctane solution. Part of the electronic spectrum of $(AcPh)Cr(CO)_3$ is shown as curve "0" in Figure 2. Orange-yellow millimolar solutions of this complex become orange-red when mixed with yellow $Eu(fod)_3$ solutions. The spectral changes accompanying incremental additions of $Eu(fod)_3$ are also presented in Figure 2. With a large stoichiometric excess of $Eu(fod)_3$, a limiting spectrum is approached in which the lowest energy band has red-shifted from ~409 to 448 nm and its absorptivity has increased by ~60%. The magnitude of the spectral shift, ~2100 cm^{-1}, far exceeds any solvent-induced shifts we have observed; for example, the lowest energy absorption band of free $(AcPh)Cr(CO)_3$ occurs at 406 and 410 nm in CH_3CN and EtOH, respectively. We explored the extent of the $Eu(fod)_3$ interaction with the other complexes of Table I. Besides $(AcPh)Cr(CO)_3$, only the benzaldehyde complex exhibited spectral changes in its MLCT band; this band shifted from 415 to 435 nm concomitant with an ~35% absorptivity increase (Table I).

We attribute the spectral changes observed on mixing the acetophenone and benzaldehyde complexes with $Eu(fod)_3$ to adduct formation wherein the oxygen atom of the arene carbonyl group coordinates to Eu. The inferred mode of adduct formation is consistent with both the red-shift in the electronic spectrum and a Cr → arene CT assignment for the lowest energy absorption band: the local presence of $Eu(fod)_3$ at the arene carbonyl group would be expected, through inductive effects, to considerably enhance the ability of the arene ligand to withdraw electron density from the metal center. The absence of corresponding changes in the other ATCr complexes examined implies that these species do not possess a site of comparable Lewis basicity.

The substantial spectral shift observed on mixing $(AcPh)Cr(CO)_3$ and $Eu(fod)_3$ permits an investigation of the adduct stoichiometry. A Job's method plot supports the presence of a 1:1 adduct. For determination of adduct formation constants, a spectrophotometric titration of an $(AcPh)Cr(CO)_3$ solution with $Eu(fod)_3$ was performed (Figure 3). A least-squares analysis gave a formation constant of 2850 ± 250 M^{-1} for a 1:1 adduct. Corresponding measurements with the benzaldehyde complex yielded a lower formation constant for a 1:1 adduct of 760 ± 75 M^{-1}. Although 1:1 adducts appear to dominate the solution composition, the possible presence of other species should be kept in mind. For example, evidence for $Eu(fod)_3$ dimers has been reported[13] and 2:1 and/or 1:2 (Cr:Eu) adducts could be present in low concentrations, as well.

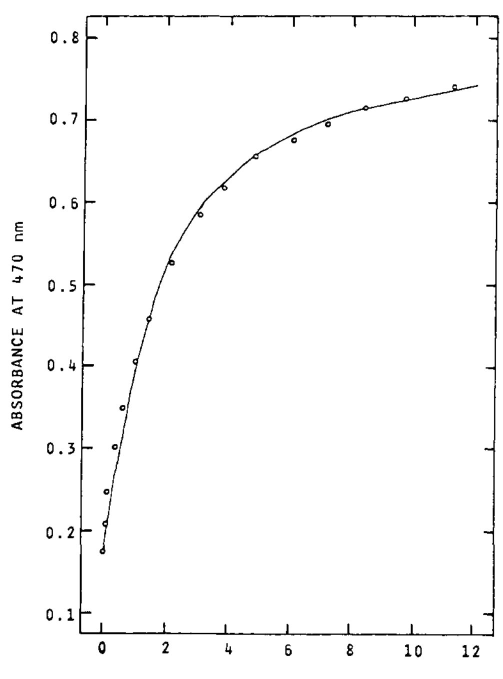

Figure 3. Spectrophotometric titration of $(AcPh)Cr(CO)_3$ with $Eu(fod)_3$ from the experiment of Figure 2. Circles represent the solution absorbance as a function of the $Eu(fod)_3$:$(AcPh)Cr(CO)_3$ mole ratio; absorbance values are uncorrected for dilution which was ~2% after 11 equiv of $Eu(fod)_3$ was added. The solid line represents the calculated titration curve based upon the formation of a 1:1 adduct between $(AcPh)Cr(CO)_3$ and $Eu(fod)_3$.

Table II. Infrared Carbonyl Stretching Bands for $(Arene)Cr(CO)_3$ Complexes, Adducts, and Photoproducts[a]

arene	band maxima, cm^{-1} (ϵ, M^{-1} cm^{-1})
aniline	1977, 1906
anisole	1982, 1910
benzene	1987, 1917
acetophenone	1996 (8100), 1937 (4500), 1926 (5400)
benzaldehyde	2002 (6700), 1944 (3900), 1935 (4300)
acenaphthene	1971, 1908, 1894
benzene photoproduct[b]	1930, 1880
acetophenone photoproduct[b]	1937, 1890
benzaldehyde photoproduct[b]	1944, 1900
acenaphthene photoproduct[b]	1908, 1856
acetophenone adduct[c]	2004 (3800), 1950 sh (2100), 1938 (3100)
benzaldehyde adduct[c]	2011, 1962 sh, 1947
adduct of acetophenone photoproduct[d]	1954, 1907

[a] Spectra recorded in N_2-saturated isooctane solution at 295 K. [b] Data obtained for photolyzed ~2 mM ATCr complex/0.36 M 1-pentene/isooctane solutions at low (≲20%) conversions. [c] Data obtained from solutions which were 2-3 mM in ATCr complex and 10-15 mM in $Eu(fod)_3$. Absorptivities are calculated as described in footnote *c*, Table I. Shoulders are indicated by "sh". [d] Data obtained for the mixture of footnote *b* when photolyzed in the presence of ~10 mM $Eu(fod)_3$.

Infrared Spectra. The infrared carbonyl stretching bands of the ATCr complexes provide additional probes of charge distri-

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[13] Porter, R.; Marks, T. J.; Shriver, D. F. *J. Am. Chem. Soc.* **1973**, *95*, 3548.

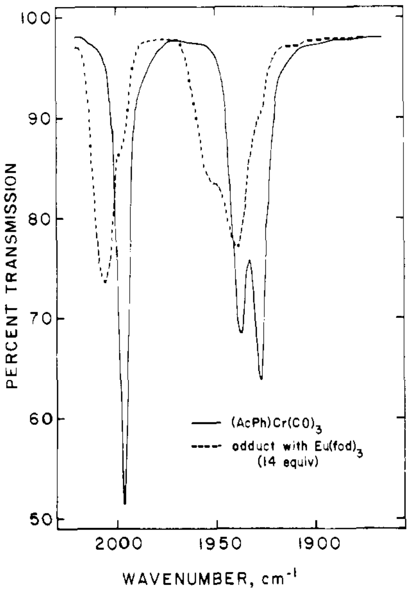

Figure 4. Infrared spectra of the carbonyl stretching region of (AcPh)-$Cr(CO)_3$ (solid line) and its adduct with $Eu(fod)_3$ (dashed line) in isooctane solution. The concentration of $(AcPh)Cr(CO)_3$ is 1.6 mM (0.022-cm path length cell).

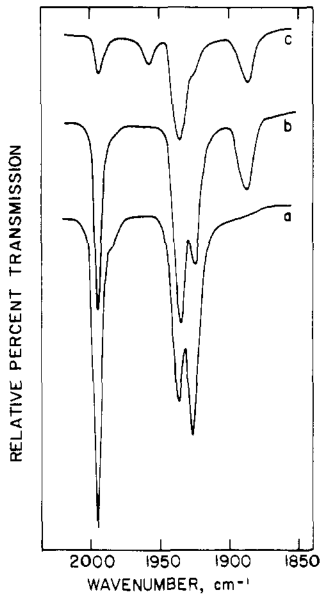

Figure 5. Infrared spectral changes in the carbonyl region accompanying the photolysis of $(AcPh)Cr(CO)_3$ in N_2-saturated 1-pentene/isooctane solution: (a) initial spectrum of 2.2 mM $(AcPh)Cr(CO)_3$ in 4% by volume (0.36 M) 1-pentene/isooctane; (b) the same solution after 30s of UV (330–380 nm) photolysis; (c) the same solution after 5 min of UV photolysis. Cell path length is 0.010 cm.

bution within the species and of adduct formation. Table II presents the positions of these bands in isooctane solution for the various ATCr complexes investigated. The general trend is for the bands to shift to higher energy as the arene substituent becomes more electron withdrawing. Such trends have been observed previously and can be ascribed to a competition between CO and the arene ligand for metal electron density: as the arene ligand accepts more electron density, less is placed in the π^* CO orbitals.[14] This reduced "back-bonding" results in increased CO stretching frequencies, ν_{CO}.

Addition of $Eu(fod)_3$ to the ATCr solutions affected the CO stretching frequencies of only the acetophenone and benzaldehyde derivatives; the other Table I complexes along with $Cr(CO)_6$ showed no evidence of spectral perturbation. Figure 4 illustrates the change in the $(AcPh)Cr(CO)_3$ IR spectrum upon the addition of a stoichiometric excess of $Eu(fod)_3$: the bands broaden and shift to higher energy by $\sim$10 cm^{-1}. Approximate positions of the adduct bands for both the acetophenone and benzaldehyde complexes are included in Table II.

The direction of the spectral shift on adduct formation supports complexation at the arene carbonyl oxygen atom: the enhanced electron-withdrawing ability of the arene as a result of adduct formation places still less electron density in the π^* CO orbitals and thereby increases ν_{CO}. We had also hoped to see complexation effects reflected in the arene CO stretching frequency which occurs at 1694 cm^{-1}. However, the $Eu(fod)_3$ complex absorbs in this spectral region, precluding comparisons between the free and bound species.

An IR spectrophotometric titration of the $(AcPh)Cr(CO)_3$ complex with $Eu(fod)_3$ was conducted for comparison with the titration based on electronic spectral changes. The IR data gave a reasonable fit to a 1:1 adduct with a formation constant of $\sim$2400 M^{-1}, gratifyingly near the value obtained from the electronic spectral results. A valuable feature of the IR spectrophotometric changes is that they permit a determination of the relative quantities of free and complexed $(AcPh)Cr(CO)_3$ for various mole ratios of $Eu(fod)_3$ to $(AcPh)Cr(CO)_3$.

Photochemistry in the Absence of $Eu(fod)_3$. Considerable precedence exists in the literature for simple photosubstitution of ATCr complexes according to eq 6.[15] A variety of entering nucleophiles, L, have been employed including pyridine, olefins, and phosphines. We chose 1-pentene as the potential entering ligand, since it has no apparent affinity for bonding to $Eu(fod)_3$; addition of $Eu(fod)_3$ to isooctane solutions of 1-pentene does not disturb the olefinic IR bands.

$$(arene)Cr(CO)_3 \xrightarrow[L]{h\nu} (arene)Cr(CO)_2L + CO \qquad (6)$$

Photolysis of N_2-saturated, isooctane solutions of (AcPh)Cr-$(CO)_3$ containing 1-pentene produced significant electronic and IR spectral changes for excitation wavelengths ranging from 313 to 600 nm. The orange-yellow solutions became orange-red upon irradiation, and new IR CO stretching bands appeared at 1937 and 1890 cm^{-1} (Figure 5 and Table II). Although we were unable to isolate the photoproduct, the positions of the new IR bands are quite similar to those reported for other $(arene)Cr(CO)_2(olefin)$ complexes;[16] the reduction in ν_{CO} would be predicted for replacement of a CO ligand with a poorer π-acceptor ligand like 1-pentene. Upon prolonged photolysis of the $(AcPh)Cr(CO)_3$/1-pentene/isooctane solution, a new peak at 1960 cm^{-1}, curve c of Figure 5, was observed. To what species this band is due was not investigated.

Quantum yield measurements were complicated by our inability to isolate the photoproduct and by the often greater absorptivity of the photoproduct at the excitation wavelengths employed (inner-filter effects). Fortunately, IR features could be employed to determine ϕ_d, the quantum yield for disappearance of the initial complex. We found that plots of the IR absorbance of $(AcPh)Cr(CO)_3$ vs. the IR absorbance of the photoproduct were linear over conversions of $\lesssim$20%. Consequently, measurements of ϕ_d were obtained in this conversion regime with the concomitant electronic spectral changes taken into account (see Experimental Section). The similar IR spectral changes observed with the benzene, benzaldehyde, and acenaphthene complexes (cf. Table II) permitted analogous measurements on these systems.

Table III summarizes ϕ_d data obtained under a variety of experimental conditions for several ATCr compounds. The quantum efficiency for disappearance of the benzene complex of 0.7 is quite high and similar to values previously reported for photosubstitution of the benzene and mesitylene complexes with pyridine and of the mesitylene complex with a maleimide.[17,18a]

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[14] Fischer, R. D. *Chem. Ber.* **1960**, *93*, 165.

[15] Reference 12, pp 78–81.

[16] (a) Trahanovsky, W. S.; Hall, R. A. *J. Organomet. Chem.* **1975**, *96*, 71. (b) Donnini, G. P.; Shaver, A. *Can. J. Chem.* **1978**, *56*, 1477.

[17] Wrighton, M. S.; Haverty, J. L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1975**, *30B*, 254.

Table III. Disappearance Quantum Yields of (Arene)$Cr(CO)_3$ Complexes[a]

arene	1-pentene concn, M	λ_{ex},[b] nm	ϕ_d (±15%)[c]
benzene	0.36	337	0.68
benzaldehyde	0.36	313	0.19
		514	0.16
acetophenone	0.36	313	0.20
		488	0.16
		514	0.18
		548	0.22
		580	0.20
		600	0.19
	0.10	488	0.18
	0.58		0.19
	0.95		0.15
acenaphthene	0.36	514	0.0011

[a] Experiments were conducted with various ATCr complexes (~1.5-3.0 mM) in N_2-saturated isooctane/1-pentene solution. The photoreaction is presumed to be that given in eq 6. [b] Excitation wavelength. [c] Quantum yield for the disappearance of the ATCr complex calculated from eq 8 as described in the Experimental Section.

Table IV. Effect of $Eu(fod)_3$ Concentration on the Disappearance Quantum Yield of (Benzene)$Cr(CO)_3$[a]

mol ratio[b] (Eu:Cr)	initial absorbance[c]	ϕ_d (±15%)[d]
0	0.752	0.68
1.0	1.04	0.66
3.0	1.61	0.69
6.0	2.48	0.63

[a] Experiments were conducted on N_2-saturated isooctane solutions which were all 1.6 mM in (benzene)$Cr(CO)_3$ and 0.36 M in 1-pentene. Excitation at 337 nm was used. The photoreaction is presumed to be that given in eq 6. [b] $Eu(fod)_3$ was added to the solution described in footnote *a* to give the indicated Eu:Cr mole ratio. [c] The initial absorbance of the indicated solution at 337 nm in the 0.10-cm path length cell employed. [d] Quantum yield for the disappearance of (benzene)$Cr(CO)_3$ calculated from eq 9 as described in the Experimental Section.

Lower, but still appreciable ϕ_d values of 0.2 were measured for the acetophenone and benzaldehyde complexes. The acenaphthene complex, however, exhibited far less efficient photoreactivity with ϕ_d ~0.001. This trend in declining ϕ_d values parallels the red-shift in what we believe to be the Cr → arene CT band and will be discussed at greater length below.

Table III also presents the effects of excitation wavelength on the measured ϕ_d values of the benzaldehyde and acetophenone complexes. For several excitation wavelengths ranging from 313 to 600 nm, no effect on ϕ_d was observed. A similar result was previously reported for the mesitylene complex.[17] The absence of a wavelength effect on ϕ_d is mechanistically important. It suggests the existence of a single relaxed reactive excited state which can be efficiently populated from upper excited states.

The effect of 1-pentene concentration on ϕ_d was examined for 488-nm excitation of (AcPh)$Cr(CO)_3$. Table III indicates that ϕ_d was unaffected by 1-pentene concentrations of 0.10–0.95 M. Similar observations were made in photosubstitution studies of the benzene complex and are consistent with the dissociative loss of CO being the primary photoprocess.[17]

Photochemistry in the Presence of $Eu(fod)_3$. The addition of $Eu(fod)_3$ to isooctane solutions of ATCr complexes and 1-pentene produced variable effects on the photoreactivity of the Cr complex. The simplest case to treat was the acenaphthene complex. Addition of 10 equiv of $Eu(fod)_3$ had no effect on the electronic (400–600 nm) and IR (2100–1800 cm^{-1}) spectral regions monitored during the photoreaction and no apparent effect on ϕ_d for 514-nm excitation: a value of ~0.001 was obtained in the presence or absence of $Eu(fod)_3$.

The photoreactivity of (benzene)$Cr(CO)_3$/$Eu(fod)_3$ mixtures was examined at 337 nm where substantial increases in solution absorbance accompany addition of $Eu(fod)_3$. However, the presence of $Eu(fod)_3$ has no effect on the IR carbonyl bands of (benzene)$Cr(CO)_3$ and its photoproduct, nor on the low-energy portion of the (benzene)$Cr(CO)_3$ electronic spectrum, thus suggesting that $Eu(fod)_3$ merely acts as a competitive light absorber. Indeed, Table IV shows that correction of ϕ_d for inner-filter effects from $Eu(fod)_3$ yields ϕ_d values of ~0.6–0.7, independent of the $Eu(fod)_3$ concentrations employed.

The most complex system was that of (AcPh)$Cr(CO)_3$/$Eu(fod)_3$ mixtures. In contrast to the benzene and acenaphthene systems, clear evidence for adduct formation was obtained from the substantial perturbation of the electronic and IR spectra of (AcPh)$Cr(CO)_3$ upon addition of $Eu(fod)_3$, as described above. Photolysis of adduct solutions led to parallel declines in the IR CO stretching bands assigned to the free and complexed (AcPh)$Cr(CO)_3$. Simultaneously, new bands appeared at 1954 and 1907 cm^{-1} in addition to the 1937 and 1890 cm^{-1} bands observed upon photolysis of $Eu(fod)_3$-free (AcPh)$Cr(CO)_3$ solutions (cf. Table II). This increase in ν_{CO} in the presence of $Eu(fod)_3$ is reminiscent of the effect of $Eu(fod)_3$ on ν_{CO} of unphotolyzed (AcPh)$Cr(CO)_3$ solutions (Table II) and suggests that the photolysis-induced bands at 1954 and 1907 cm^{-1} are due to the adduct of the photoproduct with $Eu(fod)_3$. To demonstrate that this is indeed the case, we photolyzed (AcPh)$Cr(CO)_3$/1-pentene/isooctane solutions in the absence of $Eu(fod)_3$ to ~5, 10, and 25% conversion to the presumed photoproduct, (AcPh)$Cr(CO)_2$(1-pentene). Addition of $Eu(fod)_3$ in the dark to these solutions resulted in a diminution of the 1937- and 1890-cm^{-1} photoproduct bands with the simultaneous appearance of the same 1954- and 1907-cm^{-1} bands observed on direct photolysis of the adduct mixture; the formation constant of the photoproduct-derived adduct is ~10^3 M^{-1}. When this experiment was conducted so that the Eu:Cr mole ratio and conversion extent were matched as closely as possible, very similar IR spectra were obtained. These results provide strong evidence that the course of the photoreaction is independent of the presence of $Eu(fod)_3$.

Given the common photoreaction of free and bound (AcPh)$Cr(CO)_3$, we intuitively thought that the overall disappearance quantum efficiency of (AcPh)$Cr(CO)_3$-containing species, ϕ_d, should be given by the linear combination of eq 7. In this

$$\phi_d = \alpha_{free}\phi_{free} + \alpha_{adduct}\phi_{adduct} \qquad (7)$$

expression, α_{free} represents the fraction of the initial total absorbed radiation which is absorbed by uncomplexed (AcPh)$Cr(CO)_3$; α_{adduct} is the fraction of the initial total absorbed radiation which is absorbed by the adduct; ϕ_{free} and ϕ_{adduct} are the disappearance quantum yields of the free (AcPh)$Cr(CO)_3$ and the adduct, respectively. Essentially, eq 7 gives the overall ϕ_d value as a sum of the ϕ_d values of the two components of the mixture (free and bound (AcPh)$Cr(CO)_3$), each weighted with their fractional light absorbance.

Table V presents ϕ_d values for the adduct solutions obtained with various excitation wavelengths and Eu:Cr mole ratios. For each irradiation wavelength examined, ϕ_d declines as the Eu:Cr mole ratio increases and the adduct increasingly dominates the mixture. Table V demonstrates that eq 7 accounts for this trend remarkably well: independent of the excitation wavelengths and mole ratios employed, the data consistently give a ϕ_{adduct} value of 0.017 ± 0.005, approximately 1 order of magnitude below that of the free (AcPh)$Cr(CO)_3$. We should mention that these very disparate disappearance efficiencies for the free and bound (AcPh)$Cr(CO)_3$ coupled with their parallel declines in IR absorbance imply that the adduct is quite labile.

Mechanistic Implications. Variations in ϕ_d span almost 3 orders of magnitude for the ATCr complexes investigated. In this section we examine this variation in terms of a model developed to account for similar effects in other low-spin d^6 systems. Our data will be shown to be consistent with this model which is based on the reordering of excited states. Importantly, the observed adduct

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Table V. Disappearance Quantum Yields for Solutions of $(AcPh)Cr(CO)_3$ and $Eu(fod)_3$[a]

λ_{ex},[b] nm	mol ratio[c] (Eu:Cr)	A_{tot}[d]	fraction of uncomplexed $(AcPh)Cr(CO)_3$, X_{free}[e]	α_{free}[f]	α_{adduct}[g]	ϕ_d (±15%)[h]	ϕ_{adduct}[i]
488	0	0.737	1.00	1.00	0	0.16	
	0.23	1.30	0.84	0.48	0.52	0.086	0.019
	0.44	1.96	0.65	0.24	0.76	0.052	0.017
	1.0	2.47	0.35	0.10	0.90	0.034	0.019
	1.8	2.67	0.16	0.04	0.96	0.023	0.017
	3.5	3.12	0.10	0.02	0.98	0.019	0.016
	6.0	3.34	0.05	0.01	0.99	0.014	0.012
514	0	0.198	1.00	1.00	0	0.18	
	0.12	0.370	0.90	0.48	0.52	0.096	0.018
	0.24	0.481	0.81	0.33	0.67	0.073	0.020
	0.47	0.619	0.66	0.21	0.79	0.053	0.019
	0.69	0.729	0.52	0.14	0.86	0.040	0.017
	3.1	1.40	0.10	0.01	0.99	0.017	0.015
580	0	0.0024	1.00	1.00	0	0.20	
	5.0	0.0734	0.05	0.00	1.00	0.015	0.015

[a] Experiments were conducted on N_2-saturated isooctane solutions which were 2.6, 1.8, and 2.3 mM in $(AcPh)Cr(CO)_3$ for the 488-, 514-and 580-nm experiments, respectively, and 0.36 M in 1-pentene. The photoreaction in both the presence and absence of $Eu(fod)_3$ is presumed to be that given in eq 6. [b] Excitation wavelength. [c] $Eu(fod)_3$ was added to the solution described in footnote *a* to give the indicated Eu:Cr mole ratio. [d] Initial absorbance of the solution at the indicated excitation wavelength. In the absence of $Eu(fod)_3$, this is A_0 (cf. footnote *f*). A 1.0-cm path length cell was employed for these measurements. [e] The fraction of uncomplexed $(AcPh)Cr(CO)_3$ was determined from the carbonyl bands in the IR spectra using the absorptivities given in Table II. [f] The fraction of the absorbed radiation absorbed by the uncomplexed $(AcPh)Cr(CO)_3$, calculated from the expression, $\alpha_{free} = (A_0X_{free})/A_{tot}$, with symbols defined in footnotes *d* and *e*. [g] The fraction of the absorbed radiation which is absorbed by the adduct; this is simply $(1 - \alpha_{free})$. There is some variation in the adduct absorptivities which can be calculated from the tabulated data; deviations of as much as ±20% from an average absorptivity value were observed. This may be due to contributions to the equilibrium of species other than 1:1 adducts (e.g., 1:2 and 2:1 adducts and/or $Eu(fod)_3$ dimers), as described in the text. [h] Overall disappearance quantum yield; ϕ_d is defined in eq 7 of the text and calculated as described in the Experimental Section. [i] Disappearance quantum yield for the 1:1 $(AcPh)Cr(CO)_3 \cdot Eu(fod)_3$ adduct calculated from eq 7 in the text.

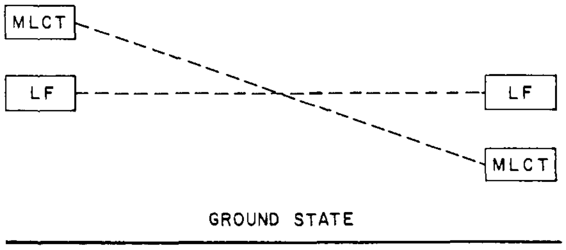
effect can be subsumed in the model.

The trend we wish to highlight in our discussion is the decline in ϕ_d in passing from $(benzene)Cr(CO)_3$ to $(AcPh)Cr(CO)_3$ to the $Eu(fod)_3 \cdot (AcPh)Cr(CO)_3$ adduct and finally to $(acenaphthene)Cr(CO)_3$. We believe that ϕ_d corresponds to photosubstitution of the parent ATCr complexes based on the IR spectroscopic changes which accompany photolysis in the presence of 1-pentene. Additionally, the independence of ϕ_d on excitation wavelength for those systems examined implicates a single reactive excited state. From numerous studies of related low-spin d^6 metal carbonyl systems,[19] a LF assignment is suggested for this photosubstitutionally labile excited state. Spectroscopic identification of LF excited states was possible in earlier studies of $W(CO)_5L$, *cis*-$W(CO)_4L_2$, $CpMn(CO)_2L$, and $CpRe(CO)_2L$ systems.[8-10] However, it was often suggested that the reactive LF excited state might not be spectroscopically detectable; for example, triplet LF excited states have been considered as the precursors to reactivity.[7,10] Although we were unable to definitively identify LF bands in the ATCr complexes studied, the crucial argument is that the energies of these excited states should be relatively independent of the arene, since the donor atoms are invariant. Similar arguments were made for the other systems reported.[7-11]

As the data in Table I indicate, arene substitution affects the position of the lowest energy absorption band in a manner consistent with its assignment as a Cr → arene CT transition. The existence of such a transition can be rationalized on the basis of the presence of a low-valent metal and a ligand with accessible π^* orbitals. Arguments have been advanced that such an excited state should not lead to metal–ligand bond cleavage: the electrostatic attraction developed in an excited state in which electron density is shifted from the metal to a ligand might, in fact, render metal–ligand bonds more difficult to rupture.[19]

In Scheme II we present a model for photoreactivity in ATCr complexes based on previous studies of low-spin d^6 systems. The key feature is that by modifying the arene ligand with more electron-withdrawing substituents, the MLCT band can be tuned to below a photoreactive LF excited state. When the MLCT state becomes lowest in energy and serves as the "energy sink" of the excited-state manifold, the photoreactivity should disappear.

Scheme II



Arene:	benzene	acetophenone	acetophenone adduct	acenaphthene
MLCT band;				
λ_{max}, nm:	375(sh)	409	448	437
ϕ_d:	0.7	0.2	0.02	0.001

Scheme II shows that the maximum of the band ascribed to a Cr → arene CT transition does generally red-shift as ϕ_d declines. The inversion involving the adduct and acenaphthene complex could be due to our use of λ_{max} values. The onset of absorption is, in fact, at higher energy for the adduct, suggesting that 0–0 energies might provide a better fit to the ϕ_d data; however, location of the 0–0 energy is hampered by the absence of adduct emission at both 295 and 77 K in methylcyclohexane. In connection with the acenaphthene complex, it is also worth mentioning that its spectral features (IR and electronic) are somewhat anomalous compared to the other ATCr complexes examined, indicating that its excited-state manifold, particularly its upper excited states, may differ substantially from the other ATCr complexes.

Of particular interest in Scheme II is the ready placement in the arene series of the $(AcPh)Cr(CO)_3 \cdot Eu(fod)_3$ adduct, assuming that the 1:1 adduct dominates the photochemistry of these mixtures. Besides excited-state reordering, however, the reduction in ϕ_d for the $(AcPh)Cr(CO)_3/Eu(fod)_3$ mixture compared to uncomplexed $(AcPh)Cr(CO)_3$ could also be ascribed to bimolecular excited-state quenching by $Eu(fod)_3$ through energy transfer. We think this is unlikely for two reasons. First, if the excited-state manifold of $Eu(fod)_3$ were populated by energy transfer, we would expect to see the characteristic pink emission of Eu(III). This emission is observable with UV excitation of the intraligand (fod-localized) band and with 578-nm excitation into an f–f band

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(19) Reference 12, pp 12–18.

but is not seen with excitation into the adduct absorption band which, in its tail, overlaps the f–f band. Second, neither the benzene nor acenaphthene complexes, which serve as the endpoints of our Scheme II data, show any evidence of interaction with $Eu(fod)_3$, either spectroscopically or with respect to their ϕ_d values. Only in that species, $(AcPh)Cr(CO)_3$, which shows clear spectroscopic evidence of adduct formation is ϕ_d perturbed. We believe that these observations in conjunction with the good fit of ϕ_d by eq 7 provide a cogent argument for participation of adducts in the excited-state reordering model of Scheme II. It should be noted, however, that our discussion of the interaction of $Eu(fod)_3$ with $(AcPh)Cr(CO)_3$ has been greatly oversimplified. The detailed manner in which $Eu(fod)_3$ influences the excited-state manifold of $(AcPh)Cr(CO)_3$ and its deactivation routes through, e.g., steric, polarization, and heavy-atom effects, remains to be established. The feature of this work we wish to emphasize is the perturbation of the excited-state properties of a substrate by adduct formation.

The environmental impact of adduct formation calls to mind similar solvent-induced effects. For example, Ford and Malouf provided evidence that solvent polarity could be used to manipulate the relative ordering of MLCT and LF states of certain $Ru(NH_3)_5L^{2+}$ (L = substituted pyridine ligand) species where presumably the two states were close in energy.[7b] The effects of solvent polarity on the luminescence and photoproducts of retinal and related systems have also been ascribed to "state switching".[20–22] Our observation of the adduct-mediated change in retinal photoproducts is interpretable with this same model wherein a π,π^* excited state crosses below an n,π^* excited state upon adduct formation.[5] That the organometallic adducts described herein can be similarly treated suggests that adduct formation may be a very general method for the perturbation of excited-state manifolds. Work in progress has as its objective the extension of these ideas to a yet broader range of species.

Experimental Section

Materials. Chromium hexacarbonyl was obtained from Pressure Chemical Company and was sublimed under vacuum (50 °C (10^{-3} torr)) prior to use. Diglyme, acetophenone, benzaldehyde, aniline, and triethyl orthoformate were obtained from Aldrich Chemical Co. and used as received. (Benzene)tricarbonylchromium(0) and (anisole)tricarbonylchromium(0) were obtained from Strem Chemical Co. and were sublimed under vacuum (50 °C (10^{-5} torr)). $(Acenaphthene)Cr(CO)_3$, a gift of Dr. K. Fivizzani and Professor P. M. Treichel, was recrystallized from isooctane. $Eu(fod)_3$ was purchased from Aldrich and dried in vacuo over P_2O_5 before use. Spectroscopic and photochemical studies were conducted in Aldrich spectrophotometric grade isooctane or methylcyclohexane which was N_2 purged and dried over 4A molecular sieves. 1-Pentene was obtained from ChemSampCo and was N_2 purged before use. Methylene chloride and Skelly B were bulk solvents purified by distillation.

Spectra. Ultraviolet and visible spectra were obtained by using a Cary 17D spectrophotometer and matched quartz cells of various path lengths. Infrared spectra were recorded on a Beckman 4230 spectrophotometer used with matched NaCl solution cells having 0.1-, 0.2-, and 1-mm path lengths. High-resolution mass spectra were obtained with a Varian AEI-MS902 spectrometer.

Optical Sources. An Osram 200-W Hg lamp in an Oriel Model 7292 housing provided ~40 and 60 mW of power centered at 313 and 546 nm, respectively; a filter solution[23] was used to isolate the 313-nm region and CS3-68, 4-72 and 1-60 Corning filters isolated the 548-nm region. An NRG 0.7-5-200 pulsed N_2 laser provided ~30 mW at 337 nm. Similar power at 488.0 and 514.5 nm was supplied by a Coherent Radiation CR-12 Ar ion laser. This laser was also used to pump a Coherent Radiation 590-03 dye laser; powers of ~200 mW at 580 and 600 nm were used from the dye laser because of low solution absorbances. To eliminate laser plasma lines, the Ar ion laser beam was passed through appropriate Oriel interference filters, each having fwhm values of 10 nm; the dye laser radiation was filtered through an Oriel Model 7240 monochromator having an 8-nm band-pass. Unexpanded laser beams (2–3-mm diameter) were used in all cases. Incident light intensities were measured with a Scientech 362 power meter (flat response 250–35 000 nm).

Syntheses. (Acetophenone)tricarbonylchromium(0), (AcPh)Cr(CO)₃. This compound was prepared from $Cr(CO)_6$ and acetophenone in diglyme by a modification of the literature method.[24] Once the red-brown oil was isolated from the reaction mixture, it was taken up in a minimal amount of methylene chloride and placed on a 2 × 20 cm silica gel chromatography column prepared with Skelly B. The column was rinsed with approximately 1 L of Skelly B until the eluent was free of $Cr(CO)_6$ and acetophenone, as determined by UV absorption spectroscopy. A 50% (v/v) mixture of methylene chloride and Skelly B was then used to develop the column. A deep red-orange band moved quickly down the column and was collected. The solvent was removed from this fraction with a rotary evaporator. The residue was a red-orange paste which was placed in a vacuum of 10^{-5} torr in order to remove traces of solvent. Subsequently, the residue was sublimed at this pressure and a temperature of 50 °C. The condensate was a slightly tacky orange solid. This solid was recrystallized from isooctane to yield a fine orange powder with an uncorrected melting range of 83.5–84.5 °C. A peak-matched high-resolution mass spectrum gave very good agreement with the theoretical *m/e* value for the parent ion. Electronic and IR spectral features are given in Tables I and II.

(Benzaldehyde)tricarbonylchromium(0). Benzaldehyde diethyl acetal, prepared by a literature method,[25] was reacted with $Cr(CO)_6$ in diglyme by the modified literature method[24] used to prepare $(AcPh)Cr(CO)_3$. However, prior to the chromatographic step, the red-brown oil was dissolved in 10 mL of 95% ethanol, and to this was added 10 mL of 2 M HCl. This mixture was stirred for 4 h, during which time the mixture became a deep red. Sodium carbonate was added, and the mixture was stirred until fizzing stopped, indicating that the acid had been neutralized. The aqueous solution was extracted with three 10-mL aliquots of diethyl ether. These red-orange ether washings were combined, and the ether was removed on a rotary evaporator. The workup then proceeded as in the synthesis of $(AcPh)Cr(CO)_3$, beginning with a chromatography on silica gel and concluding with a recrystallization from isooctane. The product was composed of bright orange needle-like crystals having an uncorrected melting range of 76–78 °C (lit.[26] 78.5–79.5 °C). A peak-matched high-resolution mass spectrum gave excellent agreement with the predicted *m/e* value for the parent ion. Electronic and IR spectral features are given in Tables I and II.

(Aniline)tricarbonylchromium(0). This species was synthesized by a method completely analogous to that used in preparing $(AcPh)Cr(CO)_3$. Its electronic and IR carbonyl bands, Tables I and II, accord well with literature values.[14,27]

Adduct Stoichiometry and Formation Constants. Job's method of continuous variations was performed by using stock solutions of $(AcPh)Cr(CO)_3$ and $Eu(fod)_3$ in isooctane, each having a concentration of 2.1 mM. Various combinations of volumes of these solutions totalling 1.5 mL were measured by using 2.0-mL graduated pipets into a 0.10-cm path length cuvette. The absorbances of the resulting solutions were measured at 470 and 510 nm. Plots of the absorbance at each of these wavelengths vs. the mole fraction of $Eu(fod)_3$ in the solution indicate a predominantly 1:1 stoichiometry for the adduct. An absorption titration was carried out on 1.5 mL of a 0.31 mM $(AcPh)Cr(CO)_3$ isooctane solution: $Eu(fod)_3$ was incrementally added to the 1.0-cm path length cell from a 0.17 M isooctane stock solution using 1.00- and 10.0-μL syringes. All manipulations were conducted in a N_2-filled glovebag. After each addition of $Eu(fod)_3$, the absorbance at 470 nm was measured. From a plot of this absorbance as a function of the $Eu(fod)_3$:$(AcPh)Cr(CO)_3$ mole ratio, formation constants were determined by using a computer program.[28] A complementary titration was conducted by following the decline in the 1996-cm^{-1} CO stretching band as $Eu(fod)_3$ was added to a 1.5 mM $(AcPh)Cr(CO)_3$ isooctane solution in a 0.22-mm path length cell. The (benzaldehyde)tricarbonylchromium(0) complex was also titrated: 3.3 and 0.33 mM isooctane solutions were titrated with 0.17 M $Eu(fod)_3$. The absorbance was monitored at 510 nm.

Photolyses. All photolysis experiments were conducted with isooctane solutions in which an ATCr complex, 1-pentene, and, in some cases, $Eu(fod)_3$ were dissolved. The solutions were prepared in a N_2-filled glovebag with use of N_2-purged isooctane and 1-pentene. The 2–3-mL

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[28] The BASIC computer program employed is supplementary material and available from the authors.

samples were irradiated in 1.0-cm path length quartz cells sealed with Teflon stoppers. During photolysis, the samples were magnetically stirred. After irradiation of the samples for various periods of time, the absorbance of the photolysate at the excitation wavelength was recorded. An aliquot of the photolysate was transferred from the cuvette to an IR cell in the N_2-filled glovebag. From the IR absorbances of the carbonyl bands, it was possible to determine the concentration of the reactants in the photolysates; generally, the highest energy CO stretching band was used. The presence of $Eu(fod)_3$ in photolyzed solutions affected the IR spectrum (carbonyl stretching region) of only the ATCr complexes which formed adducts. For mixtures of $(AcPh)Cr(CO)_3$, 1-pentene, and $Eu(fod)_3$, the CO bands due to the free Cr complex and the bands due to the adduct declined in parallel. For all the systems examined, plots of the IR absorbance of the ATCr complex (bound or free) vs. the IR absorbance of the photoproduct are linear for conversions of $\lesssim 20\%$; beyond this point, curvature increases with the extent of conversion. The initial linearity is a necessary, but not sufficient, condition to prove a 1:1 stoichiometry of the presumed photosubstitution reaction.

In determining quantum yields, we used only data from conversions of $\lesssim 20\%$ and assumed side reactions to be insignificant in these early stages of the photoreaction. The quantum yields, ϕ_d, are, strictly speaking, for the disappearance of the tricarbonyl complex. In the absence of $Eu(fod)_3$ and for situations where $Eu(fod)_3$ serves purely as a competitive light absorber, eq 8 and 9 were used, respectively; their derivation is based on a more general expression given by Nasielski et al.[18] In these equations V is the solution volume in liters; I_a, the total amount of light absorbed by the solution in einstein/second, is multiplied by the time interval, t, to give total einsteins absorbed by the solution; ϵ_A, ϵ_B, and ϵ_C are the absorptivities of the ATCr complex, $Eu(fod)_3$, and photoproduct, respectively, at the excitation wavelength; $[A]_0$ and $[A]$ are the molar initial concentration and concentration at time t of the ATCr complex; and $[B]_0$ is the concentration of $Eu(fod)_3$. Implicit in the derivation of these equations is the representation of the photoproduct concentration as $([A]_0 - [A])$; i.e., a 1:1 stoichiometry is assumed and depletion of the photoproduct through its photoreactions is treated as negligible for short photolysis periods.

$$\phi_d = \frac{V}{I_a t}\left[([A]_0 - [A])\left(1 - \frac{\epsilon_C}{\epsilon_A}\right) + \frac{\epsilon_C}{\epsilon_A}[A]_0 \ln\left(\frac{[A]_0}{[A]}\right)\right] \quad (8)$$

$$\phi_d = \frac{V}{I_a t}\left[([A]_0 - [A])\left(1 - \frac{\epsilon_C}{\epsilon_A}\right) + \frac{\epsilon_C[A]_0 + \epsilon_B[B]_0}{\epsilon_A} \ln\left(\frac{[A]_0}{[A]}\right)\right] \quad (9)$$

In the case where adduct formation obtains, the $(AcPh)Cr(CO)_3$ may disappear as either a bound or free species. The rate equation is given by eq 10, where ϵ_A and ϵ_C have been defined above, ϵ_D is the adduct absorptivity at the excitation wavelength (determined from the solution absorbance with a large excess of $Eu(fod)_3$ and assuming a 1:1 adduct stoichiometry), and [D] and [C] represent the adduct and photoproduct concentrations at time, t; ϕ_{free} and ϕ_{adduct} are the disappearance quantum efficiencies of free and bound $(AcPh)Cr(CO)_3$, respectively. Multiplication of eq 10 by $[(\epsilon_A[A] + \epsilon_D[D] + \epsilon_C[C])/(\epsilon_A[A] + \epsilon_D[D])]\,dt$ substitution from eq 7 yields eq 11, where $\alpha_{free} = \epsilon_A[A]/(\epsilon_A[A] + \epsilon_D[D])$ and $\alpha_{adduct} = \epsilon_D[D]/(\epsilon_A[A] + \epsilon_D[D])$ are the fractional absorbances of the unbound and bound $(AcPh)Cr(CO)_3$, respectively. At this point we substitute for [D] in the left-hand side of eq 11 with $K_f[A][Eu]$ from the equilibrium expression; K_f is the adduct formation constant and [Eu], the concentration of free $Eu(fod)_3$, is assumed constant, since $(AcPh)Cr(CO)_3$ and its photoproduct have similar K_f values. We also substitute for [C] with $[C] = ([A]_0 - [A] + [D]_0 - [D]) = (1 + K_f[Eu])([A]_0 - [A])$ with $[D]_0$ signifying the initial adduct concentration; we are again assuming a 1:1 stoichiometry between either the free or bound $(AcPh)Cr(CO)_3$ and the photoproduct and, initially, negligible photoreactivity of the latter. With these substitutions for [D] and [C], eq 11 integrates to eq 12. Effective values of ϵ_C are determined from the absorbance at the excitation wavelength after subtracting the contributions of the free and bound $(AcPh)Cr(CO)_3$ whose concentrations are determined from the photolysate IR spectra. All reported ϕ_d values are uncorrected for reflective losses at the cell interfaces; they are the average of at least three determinations and have associated errors of ±15%.

$$\frac{-d([A] + [D])}{dt} = \frac{I_a}{V}\left[\frac{\epsilon_A[A]}{\epsilon_A[A] + \epsilon_D[D] + \epsilon_C[C]}\phi_{free} + \frac{\epsilon_D[D]}{\epsilon_A[A] + \epsilon_D[D] + \epsilon_C[C]}\phi_{adduct}\right] \quad (10)$$

$$-d([A] + [D])\frac{\epsilon_A[A] + \epsilon_D[D] + \epsilon_C[C]}{\epsilon_A[A] + \epsilon_D[D]} = \frac{I_a}{V}[\alpha_{free}\phi_{free} + \alpha_{adduct}\phi_{adduct}]\,dt \quad (11)$$

$$-d([A] + [D])\frac{\epsilon_A[A] + \epsilon_D[D] + \epsilon_C[C]}{\epsilon_A[A] + \epsilon_D[D]} = \frac{I_a}{V}\phi_d\,dt$$

$$\phi_d = \frac{V(1 + K_f[Eu])}{I_a t}\left[([A]_0 - [A]) \times \left(1 - \frac{\epsilon_C(1 + K_f[Eu])}{(\epsilon_A + \epsilon_D K_f[Eu])}\right) + \frac{\epsilon_C(1 + K_f[Eu])[A]_0}{(\epsilon_A + \epsilon_D K_f[Eu])} \ln\left(\frac{[A]_0}{[A]}\right)\right] \quad (12)$$

Note Added in Proof. Additional examples of adduct-mediated photochemistry have been reported recently by Lewis and Oxman.[29]

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Registry No. $(C_6H_5NH_2)Cr(CO)_3$, 12108-11-1; $(C_6H_5OCH_3)Cr(CO)_3$, 12116-44-8; $(C_6H_6)Cr(CO)_3$, 12082-08-5; $(C_6H_5C(O)CH_3)Cr(CO)_3$, 12153-11-6; $(C_6H_5CHO)Cr(CO)_3$, 12170-15-9; (acenaphthene)$Cr(CO)_3$, 81434-75-5; $Eu(fod)_3$, 17631-68-4.

Supplementary Material Available: A BASIC computer program from which formation constants were calculated and the photoproduct extinction coefficients used to calculate quantum efficiencies (12 pages). Ordering information is given on any current masthead page.

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(29) Lewis, F. D.; Oxman, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 7345.