

The Primary Process in the Photochemistry of Group 6B Metal Hexacarbonyls. 2

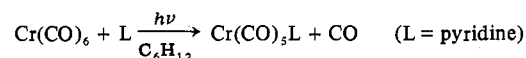
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Wavelength effect and sensitization experiments suggest that the excited singlet states of $M(\text{CO})_6$ ($M = \text{Cr}, \text{W}$) cross over to the triplet state with unit efficiency. The quantum deficit for the photosubstitution is ascribed to a radiationless decay of the excited triplet state which competes with dissociation.

Introduction

We have shown previously¹ that the quantum yield for the photosubstitution



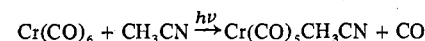
is 0.67. We describe now similar data for $\text{W}(\text{CO})_6$ and further experiments intended to give some clues to the origin of the quantum deficit.

Results

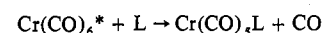
1. Effect of Ligand Concentration. A bimolecular substitution process occurring on an excited state has been considered in the photochemistry of $\text{Mn}(\text{CO})_4\text{NO}$.²

a. L = Pyridine. Our results for $\text{Cr}(\text{CO})_6$, irradiated at 292 nm in the presence of variable amounts of pyridine, are summarized in Table I. With pyridine, there is rather a slight decrease of quantum yield with rising ligand concentration; this might be due to a quenching of an excited state of $\text{Cr}(\text{CO})_6$ by pyridine or rather to a solvent effect.

b. L = Acetonitrile. In order to reach higher ligand concentrations, we have run the photosubstitution



in neat acetonitrile. The quantum yield, at 313 nm with $[\text{Cr}(\text{CO})_6] \approx 5 \times 10^{-3} \text{ M}$, was found to be 0.70 ± 0.04 . It appears quite clearly that our data are inconsistent with any major contribution from a process such as



The formation of the product occurs thus only after the photodetachment of CO from the excited state, and the efficiency 0.67 is the quantum yield for dissociation.

2. Effect of Solvent Viscosity. The quantum deficit might be assigned to an efficient cage recombination of the $\text{Cr}(\text{CO})_5$ and CO fragments; in the present case, this would be described by Scheme I, where the brackets represent a solvent cage. In this scheme, the quantum deficit is due to the deactivation of the excited state (step 1) and/or to the cage recombination (step 3). As was shown previously³ in the photolysis of iodine,²¹ cage recombination can be favored by using a more viscous solvent. This is due to the form of the rate constant $k_4 = a/\eta$, where η is the viscosity.⁴ The kinetic scheme then leads to eq

$$\phi_A^{-1}(\eta) = \phi_{\text{cage}}^{-1} \left(1 + \frac{k_3}{a} \eta \right) \quad (1)$$

1 where ϕ_{cage} stands for $k_2/(k_1 + k_2)$, i.e., the viscosity-independent quantum yield for cage formation. Results obtained with two kinds of paraffin are summarized in Table II. Extrapolation to zero viscosity according to eq 1 clearly shows that the quantum yield of dissociation— $\phi_{\text{cage}} = 0.68$ —is not very different from the value obtained for substitution in cyclohexane. Therefore, we feel safe assuming that cage recombination plays only a minor role in the quantum deficit in cyclohexane.

Table I. Effect of Pyridine Concentration on the Quantum Yield for the Photosubstitution of CO by Pyridine in $\text{Cr}(\text{CO})_6$ at 292 nm^a

[py], M ⁻¹	ϕ_A	No. of runs
2.5×10^{-4}	0.67 ± 0.04	2
2.4×10^{-3}	0.66 ± 0.05	3
2.5×10^{-2}	0.60 ± 0.05	4

^a Solvent cyclohexane; $[\text{Cr}(\text{CO})_6] = 3.5 \times 10^{-4} \text{ M}$.

Table II. Influence of Solvent Viscosity on the Photodissociation of $\text{Cr}(\text{CO})_6$ Irradiated at 313 nm^a

Solvent	η , cP	No. of runs	ϕ_A
Cyclohexane	0.97	4	0.67 ± 0.04
Paraffin I	140	2	0.51 ± 0.04
Paraffin II	237	1	0.52

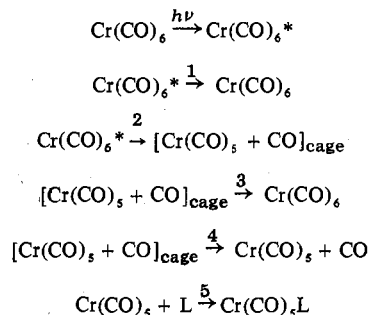
^a $[\text{Cr}(\text{CO})_6] \approx 1 \times 10^{-3} \text{ M}$; $[\text{pyridine}] \approx 2 \times 10^{-2} \text{ M}$.

Table III. Quantum Yield at 254 nm for the Photosubstitution of CO by Pyridine in $\text{W}(\text{CO})_6$ ^a

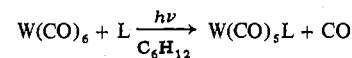
$10^3 \times$ [W(CO) ₆], M	$10^4 \times$ [py], M	ϕ_A	$10^3 \times$ [W(CO) ₆], M	$10^4 \times$ [py], M	ϕ_A
3.05	7.04	0.69	4.15	2.61	0.70
3.07	7.00	0.71	2.73	2.66	0.77

^a Solvent cyclohexane.

Scheme I



3. Quantum Yield for Photosubstitution in $\text{W}(\text{CO})_6$. Wavelength Effect. Tungsten hexacarbonyl was irradiated at 254 nm in degassed cyclohexane containing pyridine. The data of Table III show that the quantum yield for the photosubstitution



is 0.72 ± 0.04 , including the correction for all the filter effects.¹ Here again, as was noticed for chromium hexacarbonyl, there is an appreciable quantum deficit, contrary to a previous claim.⁷

$\text{W}(\text{CO})_6$ shows a weak, but distinct, absorption at 353 nm which has been assigned to a singlet-to-triplet transition induced by the heavy-atom effect⁵ (note that because of the

Table IV. Wavelength Effect on the Quantum Yield for Photodissociation of $W(CO)_6$

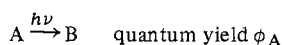
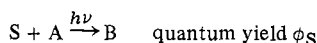
Exciting wavelength, nm	Solvent	ϕ_A
254	Cyclohexane	0.72 ± 0.05
313	Cyclohexane	0.75 ± 0.05
334	Benzene	0.72 ± 0.05
366	Benzene	0.78 ± 0.05

spin-orbit coupling, the distinction between singlet and triplet states loses part of its meaning). Table IV collects the data for irradiation at four different wavelengths. At 366 nm one can safely assume that the excited state reached is the $^3T_{1g}$ state: a crude Gaussian analysis suggests that over 90% of the light is used to populate the excited triplet state.

The constancy of the quantum yield for various wavelengths (Table IV) suggests that the same dissociating excited state is reached in all cases, probably the triplet state which dissociates with an efficiency less than 0.8. This implies that the quantum deficiency comes from a radiationless decay competing with dissociation in the triplet state. Such conclusions are sufficiently important to make energy-transfer studies desirable.

4. Energy-Transfer Studies. Vogler⁹ has measured the benzophenone-sensitized quantum yield for the photosubstitution of CO by pyridine in $Cr(CO)_6$, but without correcting for the inner-filter effects due to the hexacarbonyl and the product; this might lead to erroneous results if the reaction is allowed to proceed to too high conversions.

Let us assume a simple phenomenological scheme, allowing for a partition of light between sensitizer S and substrate A, leading to a sensitized and a direct photolysis, respectively:



where S is the sensitizer, $A = M(CO)_6$, and $B = M(CO)_5(py)$. The rates of the sensitized and direct reactions are then

$$I_0 \frac{\epsilon_S [S]}{\epsilon_S [S] + \epsilon_A [A] + \epsilon_B [B]} \phi_S$$

and

$$I_0 \frac{\epsilon_A [A]}{\epsilon_S [S] + \epsilon_A [A] + \epsilon_B [B]} \phi_A$$

respectively, where I_0 is the amount of light absorbed by the solution per unit time. The differential equation for the observed quantum yield, ϕ_{obsd} , is then

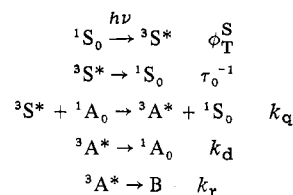
$$\phi_{\text{obsd}} = \frac{1}{I_0} \frac{d[B]}{dt} = \frac{\epsilon_S [S] \phi_S + \epsilon_A [A] \phi_A}{\epsilon_S [S] + \epsilon_A [A] + \epsilon_B [B]}$$

and leads to

$$I_0 t = \int_0^t \frac{\epsilon_A [A]_0 + (\epsilon_B - \epsilon_A) [B] + \epsilon_S [S]}{\epsilon_A [A]_0 \phi_A - \epsilon_A [B] \phi_A + \epsilon_S [S] \phi_S} d[B]$$

where $[A]_0$ is the initial concentration of $M(CO)_6$. For low conversions, $\epsilon_A [B] \phi_A$ is much smaller than $\epsilon_A [A]_0 \phi_A + \epsilon_S [S] \phi_S$, which allows a series expansion of the fraction. The exact integration leads to an expression which is too complicated to be of any practical use. The series expansion of the exact solution is identical with eq 2. Retaining terms up to the second order, the integrated equation reads

$$(\epsilon_A [A]_0 \phi_A + \epsilon_S [S] \phi_S) I_0 t = (\epsilon_A [A]_0 + \epsilon_S [S]) [B] + \left(\epsilon_B + \frac{\epsilon_A \epsilon_S [S] (\phi_A - \phi_S)}{\epsilon_A [A]_0 \phi_A + \epsilon_S [S] \phi_S} \right) \frac{[B]^2}{2} \quad (2)$$

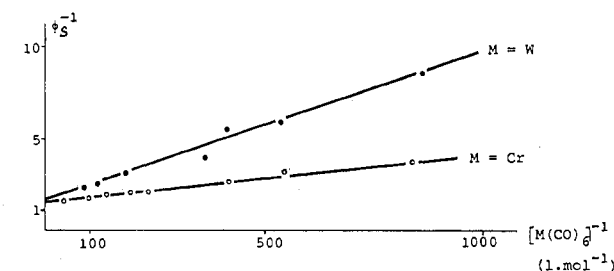
Scheme II**Table V.** Quantum Yield for the Benzophenone-Sensitized Photosubstitution in $Cr(CO)_6$ and $W(CO)_6$ ^a

$10^3 [Cr(CO)_6], M$	ϕ_S	$10^2 [W(CO)_6], M$	ϕ_S
20.7	0.685	11.2	0.456
10.2	0.592	8.49	0.440
6.81	0.556	5.40	0.366
5.09	0.493	2.71	0.248
4.18	0.485	2.41	0.184
2.35	0.405	1.85	0.173
1.81	0.341	1.16	0.079
1.20	0.261		

^a Solvent benzene; $[Ph_2CO] \approx 0.1 M$. The following values for ϵ in benzene at 366 nm were used: Ph_2CO , 64.9; $Cr(CO)_6$, 62; $W(CO)_6$, 365; $Cr(CO)_5py$, 4170; $W(CO)_5py$, 4620.

Table VI. ϕ_R^T and $k_q\tau_0$ Values for the Sensitization of $M(CO)_6 + Py$ by Benzophenone in Benzene

M	ϕ_R^T	$k_q\tau_0, L mol^{-1}$	ϕ_A
Cr	0.68 ± 0.04	584	0.69 ± 0.04
W	0.71 ± 0.07	179	0.75 ± 0.05

**Figure 1.** Dependence of ϕ_S^{-1} on $[A]^{-1}$ for the sensitization of $M(CO)_6 + py$ by benzophenone according to eq 4. $[Ph_2CO] \approx 0.1 M$; solvent benzene; $\lambda_{\text{irr}} 366 \text{ nm}$.

For photolysis at 366 nm, ϵ_A is much smaller than ϵ_B and eq 2 reduces to

$$(\epsilon_A [A]_0 \phi_A + \epsilon_S [S] \phi_S) I_0 t = (\epsilon_A [A]_0 + \epsilon_S [S]) [B] + \epsilon_B [B]^2 / 2 \quad (3)$$

For the highest concentrations of metal hexacarbonyls, filter effects are not negligible since only 83% ($M = Cr$) and 62% ($M = W$) of the light are absorbed by benzophenone. Having thus separated the direct and sensitized pathways by means of eq 3, we may turn to the analysis of the data for ϕ_S . Assuming Scheme II one finds

$$\frac{1}{\phi_S} = \frac{1}{\phi_R^T \phi_T^S} \left(1 + \frac{1}{k_q \tau_0 [A]} \right) \quad (4)$$

where $\phi_R^T = k_r / (k_r + k_d)$ is the efficiency of dissociation from the excited triplet state of $M(CO)_6$. The results for Cr and W are summarized in Table V. The values of ϕ_R^T and $k_q \tau_0$ are obtained from a plot of ϕ_S^{-1} vs. $[A]^{-1}$, assuming $\phi_T^S = 1$ ¹⁰ (Figure 1 and Table VI).

In both hexacarbonyls, we see that ϕ_R^T is very close to the value of ϕ_A , the value for direct irradiation. This supports our earlier findings which suggested that the excited states cross over to the triplet state with unit efficiency and that the dissociation occurs in the triplet state.

Table VII. Influence of Added Cr(CO)₆ on the Bimolecular Disappearance of Ketyl Radicals^a

[Cr(CO) ₆], M	k _{bimol.} , L mol ⁻¹ s ⁻¹	[Cr(CO) ₆], M	k _{bimol.} , L mol ⁻¹ s ⁻¹
0	8.8 × 10 ⁸	2.0 × 10 ⁻³	7.4 × 10 ⁸
1.3 × 10 ⁻⁵	7.7 × 10 ⁸		

^a Solvent cyclohexane; [Ph₂CO] ≈ 0.1 M; ε_{ketyl} 3320 at 545 nm.¹²

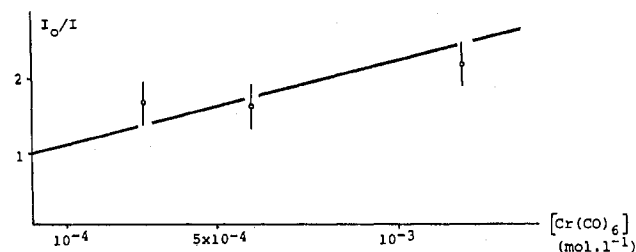


Figure 2. Stern-Volmer plot for the quenching of benzophenone phosphorescence by Cr(CO)₆ at room temperature in benzene. [Ph₂CO] = 1.9 × 10⁻² M; λ_{irr} 384 nm.

The growing recognition of radical reactions in transition-metal carbonyls led us to check whether the substitution does not involve any benzophenone ketyl radicals, which may always be formed by active impurities even in benzene solvent. Benzophenone was flashed in cyclohexane to obtain large amounts of ketyl radicals and the disappearance of radicals was monitored (λ_{max} 545 nm; lit.¹¹ λ_{max} 540 nm) with and without added Cr(CO)₆.

Should the sensitized photolysis of Cr(CO)₆ occur mainly through the action of ketyl radicals, one would expect an increase in their rate of disappearance, together with an appreciable deviation from second-order kinetics, in the presence of metal hexacarbonyl. Even with the highest (saturated) concentration of organometallic, the decay at 545 nm remains strictly second order, and no acceleration is noticed (Table VII) showing that ketyl radicals do not participate in the substitution reaction.

The efficiency of energy transfer from excited benzophenone to metal hexacarbonyl has then been estimated by an independent method. Benzophenone is known to phosphoresce in benzene at room temperature, with a low quantum yield.¹³ In the presence of Cr(CO)₆, we have observed a quenching of this emission; the data are plotted in Figure 2 according the Stern-Volmer equation.

To calculate the quenching constant, it is now necessary to know the lifetime of the excited state. The singlet excited state of benzophenone has a lifetime estimated to be 10⁻¹⁰ s.¹⁴ The triplet-state lifetime can be obtained from a Stern-Volmer plot of the luminescence quenching by naphthalene; the rate constant for this process has been found to be k_q^N = 6.3 × 10⁹ L mol⁻¹ s⁻¹.¹³ Using this value, we calculate τ₀ = 6.4 × 10⁻⁶ s. From Figure 2, one finds k_qτ = 1.3 × 10³ L mol⁻¹; assuming a transfer from S₁, we obtain k_q ≈ 10¹³ L mol⁻¹ s⁻¹, and from T₁, k_q = (2.1 ± 0.8) × 10⁸ L mol⁻¹ s⁻¹. In the first case, a dipole-dipole mechanism must be assumed to explain a quenching constant so much faster than diffusion: this seems very improbable with centrosymmetric transition-metal compounds where transitions appear with low extinction coefficients. The more realistic idea is an exchange mechanism involving ³Ph₂CO* quenched by M(CO)₆ to give ³M(CO)₆*. After correction of the lifetime of triplet benzophenone for self-quenching (k = 4.4 × 10⁵ L mol⁻¹ s⁻¹),¹⁵ the rate constants for energy transfer are found to be k_q(M = Cr) = (1.2 ± 0.3) × 10⁸ L mol⁻¹ s⁻¹ and k_q(M = W) = (3.6 ± 0.6) × 10⁷ L mol⁻¹ s⁻¹ from the quantum yield measurements, in fair agreement with (2.1 ± 0.8) × 10⁸ L mol⁻¹ s⁻¹ for M = Cr from luminescence quenching.

Another sensitizer used was triphenylene, whose triplet energy (67 kcal mol⁻¹) is close to that of benzophenone (69 kcal mol⁻¹).¹⁶ The system was irradiated at 254 nm, which means that eq 2 has to be corrected for the absorption of light by pyridine. The corresponding relation is then

$$(\epsilon_A [A]_0 + \epsilon_L [L] + \epsilon_S [S])[B] + \epsilon_B [B]^2 / 2 = (\phi_S \epsilon_S [S] + \phi_A \epsilon_A [A]_0) I_0 t$$

where L is pyridine. It must be noted that in this equation and also in eq 2, it was assumed that the sensitizer and pyridine concentration are constant; conversion must thus be kept low.

The quantum yields of sensitization were found to be much lower in this case, ranging from (3.8 ± 0.5) × 10⁻² to (3.1 ± 0.9) × 10⁻³ for respectively [Cr(CO)₆] = 1.5 × 10⁻⁴ and 1.2 × 10⁻⁵ but our data are too inaccurate to allow, by extrapolation, a reliable determination of φ_R^T. We find k_q = (1.2 ± 0.4) × 10⁵ L mol⁻¹ s⁻¹ adopting φ_T^S = 0.92;¹⁶ τ₀ was found to be 3 × 10⁻³ s for triphenylene in cyclohexane and we assumed φ_R^T to be the same as that for the other experiments, i.e., 0.68. At the present time, no explanation can be given to rationalize the difference in the k_q value obtained with these two sensitizers having similar triplet energies.

On the other hand, photosubstitution was found to be impossible to quench with biphenyl (E_T = 65 kcal mol⁻¹).¹⁶ Even with 0.8 M⁻¹ biphenyl in benzene, the quantum yield under irradiation at 334 nm gave φ_A = 0.72, which is identical with the direct-photolysis quantum yield. Naphthalene (E_T = 61 kcal mol⁻¹)¹⁶ was also found to be inefficient as quencher (2 M in benzene). Like earlier work,¹⁷ this suggests that excited states of metal hexacarbonyls are very short-lived.

Conclusions

The results show that both Cr(CO)₆ and W(CO)₆ undergo a very efficient intersystem crossing from the excited singlet manifold to an excited triplet state, which means that the singlet states are not dissociative. The quantum deficit of the dissociation step from the triplet is not due to cage recombination or to a radiative decay since the hexacarbonyls emit no phosphorescence even at 77 K.

The only process remaining is thus a radiationless transition, accompanied or not by internal rotations; such "unobservable" isomerizations have been invoked to interpret numerous quantum deficits in other areas such as the behavior of butadiene and its methyl-substituted analogues.¹⁸ Perhaps isomerization is preferable to nonradiative decay because one would expect the latter to show a heavy-atom catalysis which is not observed on going from Cr to W.

Experimental Section

Products.¹ Tungsten hexacarbonyl was sublimed. Tungsten pentacarbonylpyridine was synthesized photochemically and purified by column chromatography on alumina (elution with cyclohexane followed by cyclohexane-acetone 5:1).¹⁹ Chromium pentacarbonylpyridine was synthesized photochemically and purified by sublimation.¹⁹ Benzophenone was recrystallized twice from cyclohexane in a dark room. Paraffins were chromatographed on silica gel containing a small amount of H₄LiAl until good transparency in UV spectra was obtained. Viscosities were determined with an Ostwald viscosimeter using ethylene glycol as standard. Benzene was distilled after washing with sulfuric acid containing potassium permanganate. Triphenylene and naphthalene were sublimed. Spectrograde acetonitrile was used without purification.

Analytical Procedures.¹ All quantum yields were corrected for inner-filter effects during irradiation by use of the equation

$$\phi_A = \frac{1}{I_0 t} \left\{ \frac{\epsilon_A + \epsilon_L - \epsilon_B}{\epsilon_A} [B] + \frac{(\epsilon_L - \epsilon_B)[A]_0 - \epsilon_L [L]_0}{\epsilon_A} \ln \left(1 - \frac{[B]}{[A]_0} \right) \right\}$$

where I_{0t} is the amount of light absorbed by the sample (einstein L^{-1}); ϵ_A , ϵ_L , and ϵ_B are the molar extinction coefficients of $M(CO)_6$, ligand, and $M(CO)_5L$, respectively, at the irradiation wavelength; and $[A]_0$ and $[L]_0$ are the initial concentrations of $M(CO)_6$ and ligand and $[B]$ is the concentration of $M(CO)_5L$ at time t .

A conventional flash apparatus was used, with solutions degassed by freezing-pumping-thawing cycles. Because the final optical density was not zero, only one flash was made per solution. Filters were used to absorb light below 330 nm.

Irradiation. The same equipment was used to make irradiations of 313, 334, and 366 nm.¹ Filters used together with the monochromator are described in the literature.²⁰ For the irradiation at 254 nm, a 4-W Sylvania mercury low-pressure lamp was used with a chemical filter only.²⁰ Actinometry procedures have been previously described.¹

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Registry No. $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $Cr(CO)_5(\text{pyridine})$, 14740-77-3; $Cr(CO)_5CH_3CN$, 15228-38-3; W-

$(CO)_5(\text{pyridine})$, 14586-49-3; pyridine, 110-86-1; CH_3CN , 75-05-8; cyclohexane, 110-82-7; benzene, 71-43-2; benzophenone, 119-61-9.

References and Notes

- (1) J. Nasielski and A. Colas, *J. Organomet. Chem.*, **101**, 215 (1975).
- (2) F. Basolo and D. Keeton, *Inorg. Chim. Acta*, **6**, 33 (1972).
- (3) R. Noyes, *Z. Elektrochem.*, **64**, 153 (1960).
- (4) J. Lorand, *Prog. Inorg. Chem.*, **17** (1972).
- (5) F. Scandola et al., *J. Am. Chem. Soc.*, **97**, 4757 (1975).
- (6) A. Kirk and C. Wong, *Can. J. Chem.*, **54**, 3794 (1976).
- (7) W. Strohmeier and D. von Hobe, *Chem. Ber.*, **94**, 761 (1961).
- (8) H. Gray and N. Beach, *J. Am. Chem. Soc.*, **90**, 5713 (1968).
- (9) A. Vogler, *Z. Naturforsch.*, **25**, 1069 (1970).
- (10) H. Backstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).
- (11) H. Tsubomura et al., *Chem. Phys. Lett.*, **1**, 309 (1967).
- (12) E. Land, *Proc. R. Soc. London, Ser. A*, **305**, 457 (1968).
- (13) W. D. K. Clark et al., *J. Am. Chem. Soc.*, **91**, 5413 (1969).
- (14) S. Lym and R. M. Hochstrasser, *J. Chem. Phys.*, **51**, 2458 (1969).
- (15) L. Singer et al., *J. Am. Chem. Soc.*, **97**, 4493 (1975).
- (16) P. Engel and B. Monroe, *Adv. Photochem.*, **8**, 296 (1971).
- (17) E. Koerner von Gustorf et al., *J. Chem. Soc., Chem. Commun.*, 105 (1973).
- (18) D. Phillips et al., *Adv. Photochem.*, **5**, 329 (1968).
- (19) W. Strohmeier et al., *Chem. Ber.*, **94**, 164 (1961).
- (20) B. Muel and C. Malpiede, *Photochem. Photobiol.*, **10**, 283 (1969); J. Pitts and J. Calvert, "Photochemistry", Wiley, New York, N.Y., 1966.
- (21) We thank a reviewer who pointed out that the viscosity effect measured in the photoaquation⁵ of $Co(CN)_6^{3-}$ can be ascribed to an incorrect experimental procedure.⁶

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Electronic Structure of Alkyldynetricobalt Nonacarbonyl Clusters, $RCCo_3(CO)_9$, Based on ^{59}Co Nuclear Quadrupole Resonance Spectroscopy

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The ground-state electronic structure of $RCCo_3(CO)_9$ clusters, where R is H, CH_3 , C_6H_5 , $C_6H_5C(O)$, CF_3 , $C_2H_5C(O)O$, Cl , $CH_3C(O)O$, CH_3O , and $(C_2H_5)_3Si$ has been examined by ^{59}Co NQR spectroscopy. This series represents a range of electron-donating and electron-withdrawing substituents. The ^{59}Co nuclear quadrupole coupling constants are found to correlate with the Hammett σ function and the σ_R^- resonance parameter for the R groups. The correlation provides evidence that the apical carbon atom in the cluster transmits electronic character between the R group and the cobalt atoms by a π -resonance mechanism and not by a through-bond inductive mechanism. The ^{35}Cl resonance in $ClCCo_3(CO)_9$ when combined with other data indicates a significant amount of Cl-C multiple-bond character. Thus, NQR data at both ends of the molecule reveal electron delocalization and resonance transmission through the apical carbon atom. The benzoyl derivative has an irregular behavior in the solid state compared to the other complexes. However, its ^{13}C NMR spectrum gives evidence of a normal structure in solution.

Introduction

The class of metal cluster compounds known as alkyldynetricobalt nonacarbonyls, $RCCo_3(CO)_9$, has attracted considerable attention in recent years. Much of this interest stems from the variety of R groups which can be bonded to the methylidyne carbon atom and their encumbant chemistry. The syntheses, reactions, and physical properties of these complexes have been compiled in several reviews.¹⁻³

Our interest in these complexes is directed toward understanding the ground-state electronic structure in the cluster.⁴ The approach to this problem has been to investigate the ^{59}Co nuclear quadrupole resonance spectra as a function of variation in the R group through a range of strongly electron-withdrawing to strongly electron-donating groups. The substituents studied are second-row-element-based with the exception of the chloro- and triethylsilylmethylidyne tricobalt nonacarbonyl. By examining how the cobalt atoms respond to "push-pull" electronic effects, additional information on the bonding characteristics of the Co_3-C-R framework has been experimentally obtained. The only picture of bonding in these complexes which is consistent with the results is one which allows significant π -electronic transmission through the apical carbon atom in the cluster.

Experimental Section

Syntheses. The alkyldynetricobalt nonacarbonyls used in this work have been reported before. Synthetic procedures reported in the literature were followed for $RCCo_3(CO)_9$, R = H,⁵ Cl,⁵ Br,⁵ CH_3 ,⁵ $C(O)CH_3$,⁵ $C(O)OC_2H_5$,⁵ OCH_3 ,⁵ $C(O)C_6H_5$,⁵ CF_3 ,⁶ C_6H_5 ,⁷ CH_3CHOH ,⁸ CO^+ ,⁹ $C_5H_5FeC_5H_4C(O)$,⁹ $CH_3C(O)O$,¹⁰ and $C(O)N(CH_3)_2$.¹¹ The $(C_2H_5)_3Si$ derivative was obtained from Professor D. Seyferth. All solvents used were dried and degassed, and all reactions were carried out under an atmosphere of nitrogen in Schlenk ware. The only exception was the CF_3 derivative, for which autoclaving was necessary. In most cases, the purification of the products was different from that reported, however.

Dry column chromatography¹² was found to be a simple and useful method for purifying these complexes. This technique has the advantage of retaining the resolution of thin layer chromatography but allowing a preparative-scale separation. In general, the support (silica gel or alumina) was packed into a nylon column having dimensions of approximately 1.5 × 25 in. with a glass wool plug and vent holes at the bottom. The sample to be separated (1-3 g) was dissolved in a minimum amount of solvent, and a small amount of support was added (about 5-7 g). The solvent was removed under vacuum. The resulting powder was layered on top of the support in the nylon column and then covered with a layer of sand. The column was developed in the normal manner, except that separation was complete when the solvent front reached the bottom of the column. The amount of solvent