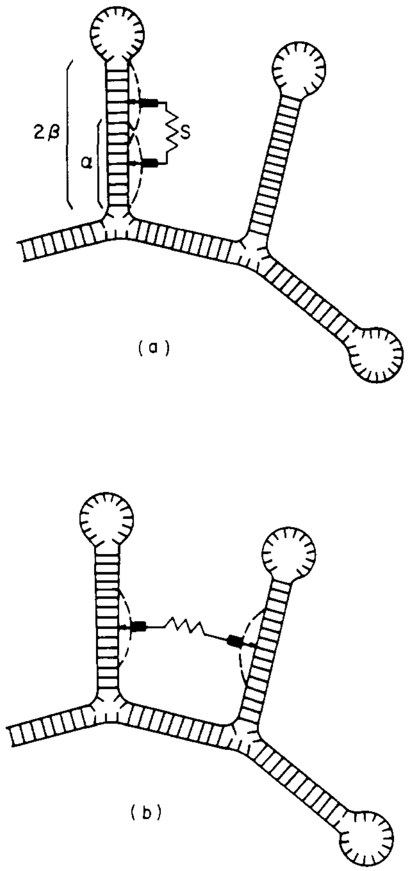

Figure 2. Schematic representations of possible modes of binding of the bis(platinum) complexes with poly(dA-dT). Here α and β are the numbers of base pairs stabilized per platinum and S is the base pair span. In (a) both platinums bind the same stem and the two α regions overlap whereas in (b) the bis(platinum) complex bridges two adjacent hair-pin stems.

increasing S values for **2** as the BP/M ratio increases may indicate that **2** binds the polynucleotide *via additional pathways* which are different from the presumed chelation on the same stem of the double helix (cf. Figure 2a). Since it is known that poly(dA-dT) forms hair-pin loops, one possibility is that **2**, which lacks the anchoring NH_2^+ groups, may bridge across two hair-pin loops (cf. Figure 2b) such that, at high BP/M ratios, each platinum can cover relatively more base pairs on different hair-pin stems thereby giving rise to higher β and hence larger S values.

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Registry No. **1**, 56815-80-6; **2**, 78656-89-0; **3**, 78656-90-3; **4**, 78656-91-4; K_2PtCl_4, 10025-99-7.

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Photosubstitution Reactivity of Carbon Disulfide Complexes of Zerovalent Iron

Claude C. Frazier,* Ronald F. Kline, and David D. Barck

Received May 20, 1981

Transition-metal η^2-CS_2 complexes have received considerable attention in recent years.[1] Much of this interest derives from the synthetic utility of carbon disulfide complexes in preparing thiocarbonyl compounds, dithiolene iron complexes, and carbon disulfide-bridged binuclear species.[2-4] Reports of the dynamic behavior of the η^2-CS_2 ligand in mononuclear complexes, the fluxional nature of some CS_2-bridged molecules, and the superior π-acceptor strength of the η^2-CS_2 ligand indicate a concomitant interest in the coordinative bonding of the carbon disulfide ligand.[4a,5,6] While understanding of the thermal chemistry and solution dynamics of carbon disulfide compounds has progressed, there has not been a parallel development of the photochemistry of transition-metal carbon disulfide complexes. In this context, we wish to report the first photochemical study of this interesting class of compounds.

Table I. Wavelength Dependence for Quantum Efficiency of $Fe(\eta^2\text{-}CS_2)(CO)_2(PR_3)_2$ to $Fe(CO)_3(PR_3)_2$ Conversion[a]

	$10^2\Phi$		
starting complex	430 nm	366 nm	313 nm
$Fe(\eta^2\text{-}CS_2)(CO)_2[P(OMe)_3]_2$	2.7	6.4	8.4
$Fe(\eta^2\text{-}CS_2)(CO)_2[PEt_3]_2$	3.4	5.7	8.8

[a] 0.03 M metal complex in CO-saturated toluene. Quantum yields are ±10%.

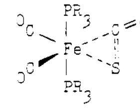
Experimental Section

The $Fe(\eta^2\text{-}CS_2)(CO)_2(PR_3)_2$ complexes were prepared by the published method.[1c] PEt_3 and $P(OMe)_3$ were obtained from Strem Chemicals, Inc., and used without further purification. Solvents were purchased from commercial sources and were bubbled with nitrogen before use. Air-sensitive compounds and solutions were handled under nitrogen with the use of Schlenk equipment in conjunction with a vacuum inert-gas manifold.

The photolysis apparatus consisted of a 450-W Hanovia mercury lamp with λ_{irr} isolated with appropriate glass filters and filter solutions. Irradiations were performed in Schlenk tubes. Light intensities were measured by ferrioxalate actinometry. Product yields on irradiation were monitored by infrared spectroscopy using a Beckman IR 12 spectrophotometer. UV-vis solution spectra were obtained with a Beckman ACTA II spectrophotometer.

Results and Discussion

The iron(0) complexes $Fe(\eta^2\text{-}CS_2)(CO)_2(PR_3)_2$ (R = alkyl or alkoxy) (**1**) are among the best characterized of the η^2-carbon disulfide transition-metal complexes. They are relatively easy to prepare, and most members of the $Fe(\eta^2\text{-}CS_2)(CO_2)(PR_3)_2$ series are stable in deoxygenated solvents. The axial phosphines of **1** are labile with the less basic and/or sterically hindered phosphines being readily replaced with good nucleophiles.[1c,d] In contrast to the ease of phosphine replacement, displacement of η^2-coordinated carbon disulfide with phosphines or carbon monoxide is generally not observed



R = alkyl or alkoxy group
1a: Et
1b: (OMe)
1c: Ph

1

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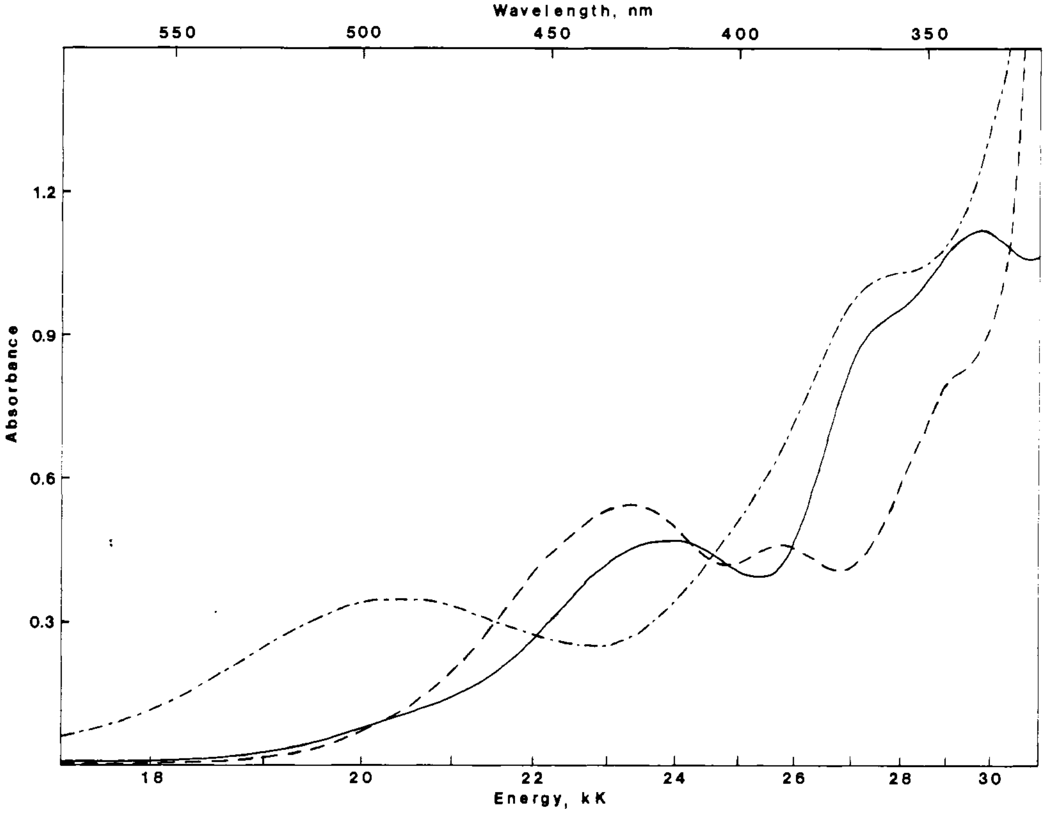


Figure 1. Electronic absorption spectra of Fe(η^2-CS_2)$(CO)_2[P(OMe)_3]_2$ (—), Fe(η^2-CS_2)$(CO)_2(PEt_3)_2$ (--), and Fe(η^2-CS_2)$(CO)_2(PPh_3)_2$ (---) in toluene. Spectra were not recorded at the same concentration.

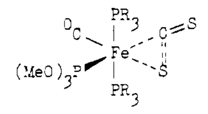
as a thermal step in ambient-temperature solutions of **1**.[1c,7] We have observed that irradiation of toluene solutions of **1** in the presence of carbon monoxide or tertiary phosphine, PR_3, effects carbon disulfide displacement, producing $Fe(CO)_3(PR_3)_2$ or $Fe(CO)_2(PR_3)_3$, respectively. Photosubstitution with carbon monoxide is clean, quantitative, and wavelength dependent (Table I). Quantum yields for Fe(η^2-CS_2)$(CO)_2(PEt_3)_2$ and Fe(η^2-CS_2)$(CO)_2[P(OMe)_3]_2$ are similar and indicate increased efficiency of CS_2 loss at shorter wavelengths. A comparable wavelength effect is noted for the formation of $Fe(CO)_2(PEt_3)_3$ from Fe(η^2-CS_2)$(CO)_2(PEt_3)_2$ and PEt_3.

Quantum yields (Φ) for formation of $Fe(CO)_2(PEt_3)_3$[8] are as follows: at 430 nm, 3.3×10^{-2}; at 366 nm, 7.2×10^{-2}; at 313 nm, 1.0×10^{-1}.

The similarity of CO and phosphine substitution quantum yields for Fe(η^2-CS_2)$(CO)_2(PEt_3)_2$ is probably fortuitous. The concentration of CO-saturated toluene at 25 °C is approximately 8×10^{-3} M, giving a ligand to metal complex ratio of less than 0.3:1. While we have not studied the CO-concentration dependence of the quantum yields, we have found that quantum yields for η^2-CS_2 replacement with tertiary phosphines are phosphine-concentration independent with ligand concentrations of 0.11 down to 0.02 M, where the quantum yields begin to diminish. The even smaller concentration of CO might similarly be expected to lead to smaller quantum yields for replacement of η^2-CS_2 with CO than the values which would be obtained with excess ligand. Since good π-acceptor ligands, e.g., CO, which can stabilize an equatorial position, are expected to be better replacements for the displaced η^2-CS_2 than PEt_3, it is likely that the similar quantum yields observed in this study are partly the result of dissimilar ligand concentrations.

In an unirradiated, ambient temperature, toluene solution of **1b** and excess $P(OMe)_3$, η^2-CS_2 loss is not observed. Instead, an equatorial CO group is replaced by a $P(OCH_3)_3$ ligand, producing Fe(η^2-CS_2)$(CO)[P(OMe)_3]_3$ **2b** (ν(CO), in toluene, 1929 cm^{-1}). A similar reaction between Fe(η^2-CS_2)$(CO)_2[P(OMe)_3]_2$ and PMe_2Ph in refluxing CH_2Cl_2 producing Fe(η^2-CS_2)$(CO)[P(OMe)_3][PMe_2Ph]_2$ (ν(CO), in THF, 1904 cm^{-1}) has been reported.[1c] When solutions of **1b** and $P(OMe)_3$ are irradiated, **2b** and **3b** are formed.[9] By correcting for the thermal reaction, it is seen that the formation of **2b** has been accelerated by irradiation. At 366 nm we have measured a quantum yield of 8.9×10^{-2} (±15%) for **3b** formation and a corrected quantum yield of 1.1×10^{-1} (±15%) for **2b** production.

Equatorial CO loss is not observed thermally in toluene solutions of **1a** and $P(OMe)_3$. On irradiation with 366-nm light, both CS_2 and CO replacements are observed, yielding **2a** (ν(CO), in toluene, 1914 cm^{-1}) with a quantum yield of



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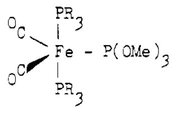

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a: R = Et

b: R = OMe

8×10^{-2} and **3a** with a yield of 10^{-1}.[9] We are currently examining the wavelength dependence of CO and CS_2 loss as

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(7) We have noted that CO replaces η^2-CS_2 in **1c** in a slow thermal step in toluene. A similar observation has been reported for **1c** in acetone solution in ref 1d. The enhanced lability of **1c** in solution, which has been commented on in ref 1c,d, is undoubtedly a factor in the ease with which η^2-CS_2 is replaced by CO in this complex.

(8) Experimental runs were 0.024 M Fe(η^2-CS_2)$(CO)_2(PEt_3)_2$ in toluene, with a ligand/metal complex ratio of 2.8:1. Samples were stirred during irradiation.

(9) A. Reckziegel and M. Bigorgne, *J. Organomet. Chem.*, **3**, 341 (1965), reported ν(CO) in hexadecane for **3b** as 1937.2 and 1878.6 cm^{-1} and for **3a** as 1989.1 and 1838.9 cm^{-1}. In the irradiated toluene solutions containing **3b** and **3a**, the peaks associated with these complexes were observed at 1935, 1872 cm^{-1} and 1895, 1834 cm^{-1}, respectively.

a function of entering ligand and of the nature of the axial phosphines.

In Figure 1, the room-temperature, UV–vis toluene-solution spectra of complexes **1a–c** are presented. The lowest energy absorptions range from 489 nm for **1c** to 417 nm for **1b**, with the low energy band for **1a** at 428 nm. The position of the lowest energy transition in each of these complexes is relatively insensitive to solvent medium. This fact, as well as the moderate ϵ of this absorption, suggests that this band is predominently metal-centered d–d in origin. Several metal-centered d–d transitions are possible for the idealized C_{2v} structure which results from viewing the η^2-CS_2 group as a monodentate, spherical ligand. The increased quantum efficiency with increasing frequency of irradiating light may be the result of excitation of higher energy d–d states or may represent enhanced lability due to involvement of charge-transfer excited states. We have initiated detailed spectroscopic studies of **1** and related complexes in order to provide a more complete assignment of the lowest energy bands.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Penrose Fund of the American Philosophical Society, and the Graduate School of the University of Minnesota for the support of this research.

Registry No. **1a**, 72557-49-4; **1b**, 64424-66-4; **1c**, 64424-68-6; **2a**, 78672-45-4; **2b**, 78672-46-5; **3a**, 78685-04-8; **3b**, 78685-05-9; $Fe(CO)_2(PEt_3)_3$, 14837-55-9.

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Kinetics and Mechanism of Base Hydrolysis of (αβ*S*)-(Salicylato)(tetraethylenepentamine)cobalt(III) Ion

A. C. Dash*[1] and G. M. Harris*

Received April 16, 1981

Previous studies[2-4] have dealt with the kinetics of acid and base hydrolysis of *cis*-(ammine)(substituted salicylato)bis(ethylenediamine)cobalt(III) complexes. It was noted that the phenoxide form of such complexes, $[N_5CoOCOC_6H_3O(X)]^+$ (X = H, 5-Br, 5-SO_3^-, 5-NO_2, 3-NO_2 for N_5 = *cis*-$(en)_2(NH_3)$ and X = H for N_5 = $(en)_2$(im-H)),[5] aquates $\sim 10^3$ times faster than the corresponding phenol form under comparable conditions. Considering the overall charge of the leaving group, this appears to be an unusual reactivity contrast. Further, the observed linear correlation between log k_{aq} and pK_{OH} of the substituted salicylato complexes, *cis*-$[Co(en)_2(NH_3)(OCOC_6H_3O(X))]^+$ (where k_{aq} is the aquation rate constant for the phenoxide form), with slope = 0.98 ± 0.03 indicates that the basicity of the unbound phenoxide group of the complex governs the rate of elimination of salicylate ligand from the cobalt(III) center.[3] The activation parameters for this path are consistent with a Co–O bond-breaking mechanism rather than the phenoxide-assisted hydration of the acyl carbon followed by ester type (i.e., C–O) cleavage. These lines of evidence suggest that the unbound phenoxide group generates the amine conjugate base, *cis*-$[Co(en)_2(NH_2)OCOC_6H_3OH(X)]^+$, in an intramolecular acid–base equilibrium step. Such a species would be expected to aquate much faster than its conjugate-acid analogue.

It is well-known that the rates of aquation of N_5CoCl^{2+} complexes (N_5 = $(NH_3)_5$, $(en)_2(NH_3)$, (triethylenetetramine)(NH_3), and tetraethylenepentamine) decrease significantly with increasing chelation of the cobalt(III) center.[6] One would therefore anticipate that, in the absence of the internal conjugate-base mechanism referred to earlier, the phenoxide form of (salicylato)(tetraethylenepentamine)cobalt(III) species should undergo aquation at a rate slower than the corresponding $(en)_2(NH_3)$ complex. To our surprise, the present study shows that the tetren phenoxide complex undergoes aquation within the stopped-flow time scale, very much faster than any of the (salicylato)(amine)cobalt(III) complexes studied so far. Base hydrolysis also occurs much more rapidly with the tetren species than with the salicylato analogues studied earlier but takes place considerably more slowly than with a number of halogen and pseudohalogen congeners containing the same amine–cobalt moiety.

Experimental Section

Materials. Tetraethylenepentamine (tetren) was used as obtained from Matheson Coleman and Bell. All other chemicals were of reagent grade, and the distilled water was further deionized before use in a mixed-bed ion-exchange column. Sodium perchlorate was used for ionic strength adjustment.

Preparation and Characterization of Compounds. (αβ)-Chloro(tetraethylenepentamine)cobalt(III) perchlorate was prepared as described by House and Garner.[7-9] (αβ*S*)-[Co(tetren)($OCOC_6H_4OH$)]$(ClO_4)_2$[10] was prepared from this chloro complex following the method described earlier for the preparation of *cis*-ammine(salicylato)bis(ethylenediamine)cobalt(III) perchlorate.[11] Anal. Calcd for $[Co(C_8N_5H_{23})(CO_2C_6H_4OH)](ClO_4)_2$: C, 30.81; H, 4.83; N, 11.98; Co, 10.08. Found:[12] C, 30.74; H, 4.86; N, 11.88; Co, 10.06. The spectral parameters for the complex measured by means of a Cary 118 spectrophotometer are as follows [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 491 (170) and 298 (4318) in 0.1 M $HClO_4$ medium. These may be compared to the corresponding data for (salicylato)pentaamminecobalt(III) ion [λ_{max},nm (ϵ, M^{-1} cm^{-1}): 510 (82.4), 298 (4417);[13] 503 (76.0), 298 (4400)[14]] and for *cis*-(ammime(salicylato)bis(ethylenediamine)cobalt(III) ion [500 (113), 298 (4474)[11]].

Rate Measurements. The kinetics of the hydrolysis of the salicylato complex was investigated at 20 °C $\leq t \leq$ 35 °C over the range of 0.01 M $\leq$ [OH] $\leq$ 0.9 M (I = 1.0 M). The rate measurements were made at 380 nm on a computerized Durrum Model 110 stopped-flow assembly. One of the syringes of the apparatus contained the appropriate concentration of NaOH adjusted to I = 2 M, whereas the other syringe contained a complex solution in 0.001 M $HClO_4$ medium. Runs were made under pseudo-first-order conditions in the usual way with $[complex]_T$ = (3.6–5.0) × 10^{-4} M. The observed pseudo-first-order rate constants were calculated by use of a least-squares program and are reported as the mean of at least five kinetic runs.

Results and Discussion

In acidic solution (pH ~4) there was no evidence of hydrolysis of the complex during a period of up to 10 h at 25

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