Table II. Comparison of Quantum Yields for the Ligand Field Excitation of Rh(III) and Ir(III) Complexes[a]

$$M(NH_3)_5L^{n+} + H_2O \xrightarrow[\Phi_L]{h\nu} M(NH_3)_5H_2O^{3+} + L$$

Complex	Ir(III)		Rh(III)	
	λ_{irr}, nm	Φ_L, mol/einstein	λ_{irr}, nm	Φ_L, mol/einstein
$M(NH_3)_6{}^{3+}$	313	0.09	313	0.075[b]
	254	0.082	254	0.07[b]
$M(NH_3)_5H_2O^{3+}$	313	0.42	313	0.43[c]
$M(NH_3)_5Cl^{2+}$	313	0.13	280-380	0.12-0.16[d]
		0.02[e]		$\leqslant 10^{-3}$ [e]

[a] In 25 °C, acidic aqueous solution. [b] Reference 12. [c] Reference 13. [d] T. L. Kelly and J. F. Endicott, *J. Phys. Chem.*, 76, 1937 (1972). [e] Φ_{NH_3} from $M(NH_3)_5Cl^{2+}$.

Table III. Φ_{NH_3} Values for the Ligand Field Excitation of $M(NH_3)_6$[a]

$$M(NH_3)_6 + H_2O \xrightarrow{h\nu} M(NH_3)_5H_2O + NH_3$$

M	λ_{irr}, nm	Φ_{NH_3}, mol/einstein	M	λ_{irr}, nm	Φ_{NH_3}, mol/einstein
Co(III)	514	0.0002[b]	Ir(III)	313	0.09
	488	0.0003		254	0.082
	365	0.005[c]	Ru(II)	313	~0.2[e]
Rh(III)	313	0.075[d]	Cr(III)	380-600	0.30[f]
	254	0.07[d]		320-410	0.36[f]

[a] In 25 °C, acidic aqueous solution. [b] Reference 15. [c] Reference 2, p 231. [d] Reference 12. [e] R. E. Hintze, Ph.D. Dissertation, University of California, Santa Barbara, Calif., 1974. [f] Reference 2, p 96.

photolysis of $Ir(NH_3)_5H_2O^{3+}$ and $Ir(NH_3)_5Cl^{2+}$. However, in contrast to similar cobalt(III) systems,[15] the ligand preferentially labilized is the one occupying the weaker position in the spectrochemical series (i.e., H_2O or Cl^-).

The quantitative similarity between Φ_L values for analogous Ir(III) and Rh(III) complexes (Table II) is somewhat surprising. The only difference of consequence is the modest NH_3 photoaquation noted for $Ir(NH_3)_5Cl^{2+}$. We have also observed qualitatively that, as with the Rh(III) analogues, NH_3 aquation is the dominant photoreaction resulting from LF excitation of $Ir(NH_3)_5Br^{2+}$ and $Ir(NH_3)_5I^{2+}$.

Thermal substitution reactions for iridium(III)-ammine complexes are generally much slower than for the Rh(III) analogues.[10,14] In addition, limited data suggest that the measured lifetimes of iridium(III)-ammine ligand field excited states are shorter than those of the equivalent Rh(III) states.[17] Thus, the quantum yield similarities between the Ir(III) and Rh(III) systems may be fortuitous, although moderate activity toward photoaquation is common for LF excitation of hexacoordinate metal complexes. For example, comparison of Φ_{NH_3} values for various hexaammine complexes (Table III) shows that of the systems [Ru(II), Co(III), Rh(III), Ir(III), and Cr(III)] for which quantitative data are available, $Co(NH_3)_6{}^{3+}$ is the only one which does not display moderate activity toward photosubstitution under ligand field excitation in aqueous solution. One might argue that the lower energy of Co(III) LF states may provide alternative pathways for rapid nonradiative deactivation. However, while there is little evidence regarding how the mechanisms for photosubstitution differ among these ions, it is noteworthy that recent studies[18] of the tripositive metal-ammine complexes $M(NH_3)_5H_2O^{3+}$ (M = Cr(III), Co(III), Rh(III), or Ir(III)) indicate that the mechanism of the thermal substitution reaction for Co(III) is different (interchange dissociative) from those (interchange associative) of the other three. Nonetheless, the connecting points between excited-state and ground-state reaction mechanisms are poorly understood, and it is not unlikely that the low photoactivity of cobalt(III)-ammine complexes to ligand field excitation is little related to those properties which differentiate the ground-state substitution mechanisms.

Acknowledgment. This work was partially supported by the National Science Foundation (Grant GP-36643X). M.T-S. wishes to acknowledge a fellowship from the Ministry of Science and Higher Education of Iran. P.C.F. wishes to thank the Research School of Chemistry, The Australian National University, for a Visiting Fellowship and the Australian-American Educational Foundation for a travel agent during the course of this research. We especially thank Dr. Alan Sargeson and Dr. D. A. Buckingham of The Australian National University for their guidance and assistance in measuring the solvent-exchange quantum yields and G. Turner and F. D. Bergerson of the CSIRO Division of Plant Industry (Canberra, Australia) for determining the CO_2 isotropic enrichments. We thank the Matthey Bishop Co. for a loan of iridium used in this study. Dr. J. D. Petersen (presently at Kansas State University) participated in the initial experiments of this study in this laboratory.

Registry No. $Ir(NH_3)_6{}^{3+}$, 24669-15-6; $Ir(NH_3)_5H_2O^{3+}$, 29589-08-0; $Ir(NH_3)_5Cl^{2+}$, 29589-09-1.

References and Notes

(1) Camille and Henry Dreyfus Foundation Teacher-Scholar, 1971-1976.
(2) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, London, 1970.
(3) A. W. Adamson and P. D. Fleischauer, Ed., "Concepts of Inorganic Photochemistry", Wiley, New York, N.Y., 1975.
(4) P. C. Ford, J. D. Petersen and R. E. Hintze, *Coord. Chem. Rev.*, **14**, 67 (1974).
(5) M. M. Muir and W. L. Huang, *Inorg. Chem.*, **12**, 1930 (1973).
(6) H. D. Gafney, J. L. Reed, and F. Basolo, *J. Am. Chem. Soc.*, **95**, 7998 (1973).
(7) H. H. Schmidtke, *Inorg. Chem.*, **5**, 1682 (1966).
(8) G. W. Watt, E. P. Helverston, and L. E. Sharif, *J. Inorg. Nucl. Chem.*, **24**, 1067 (1962).
(9) H. H. Schmidtke, *Inorg. Synth.*, **12**, 243 (1970).
(10) E. Borghi and F. Monacelli, *Inorg. Chim. Acta*, **5**, 211 (1971).
(11) (a) R. E. Hintze and P. C. Ford, *Inorg. Chem.*, **14**, 1211 (1975); (b) *J. Am. Chem. Soc.*, **97**, 2664 (1975).
(12) J. D. Petersen and P. C. Ford, *J. Phys. Chem.*, **78**, 1144 (1974).
(13) J. D. Petersen and P. C. Ford, *Inorg. Chem.*, **14**, 1404 (1975).
(14) F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions", Wiley New York, N.Y., 1967.
(15) R. A. Pribush, C. K. Poon, C. M. Bruce, and A. W. Adamson, *J. Am. Chem. Soc.*, **96**, 3027 (1974).
(16) M. J. Incorvia and J. I. Zink, *Inorg. Chem.*, **13**, 2489 (1974).
(17) M. K. DeArmond and J. E. Hillis, *J. Chem. Phys.*, **54**, 2247 (1971).
(18) S. B. Tong and T. W. Swaddle, *Inorg. Chem.*, **13**, 1338 (1974).

Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

Photochemistry of Dithiocarbamato Complexes. 1. Photolysis in Chlorine-Containing Solvents

G. L. Miessler, G. Stuk,[1a] T. P. Smith,[1b] K. W. Given, M. C. Palazzotto, and L. H. Pignolet*

Received November 3, 1975 AIC507918

There have been only two reports on the photochemistry of metal dithiocarbamato complexes.[2] One of these involved the reversible photobleaching of tris(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(IV) bromide, $[Ni(Bu_2dtc)_3]Br$, in acetonitrile solution according to eq 1.[2a] This reaction which also

$$2Ni(Bu_2dtc)_3{}^+ + 2Br^- \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}} Ni(Bu_2dtc)_2 + NiBr_2 + 2(Bu_2dtc)_2 \quad (1)$$

occurs thermally suggests that photoreduction of the metal

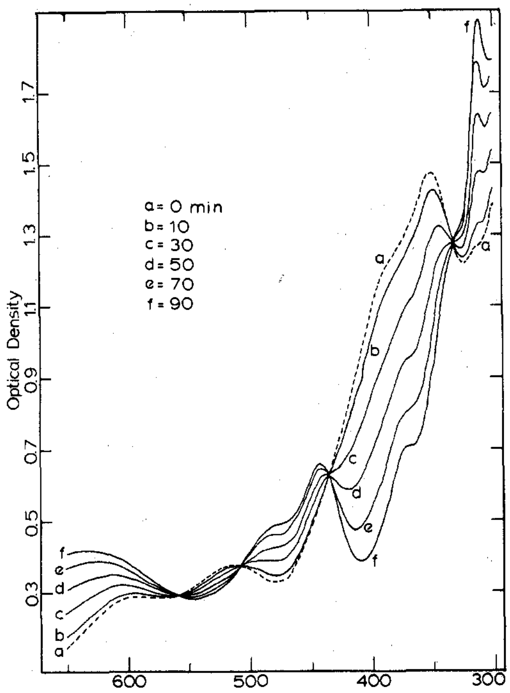


Figure 1. Spectral changes during photolysis at 265 nm of 1.19 × 10^{-4} M Fe(Et$_2$dtc)$_3$ in C$_6$H$_5$Cl solution. Lines a and f are due to Fe(Et$_2$dtc)$_3$ and ClFe(Et$_2$dtc)$_2$, respectively.

accompanied by oxidation of the ligands to thiuram disulfide, (R$_2$dtc)$_2$, may be a general reaction of dithiocarbamatometal complexes. For certain metals the resulting reduced and coordinatively unsaturated metal complex is expected to be reactive toward various electrophilic ligands. With this as a working premise we embarked on a general study of the photochemistry of transition metal complexes with sulfur donor ligands. Several interesting photochemical reactions of Fe(Et$_2$dtc)$_3$ and Ru(Et$_2$dtc)$_3$ were observed and are reported here.

During our studies on the redox and stereochemical properties of M(R$_2$dtc)$_3$ complexes[3-5] it was noted but not published that dilute solutions of Fe(Et$_2$dtc)$_3$ in CHCl$_3$ slowly turned from brown to green in the presence of laboratory light. The color change could be prevented if the solutions were kept in the dark. Detailed analysis of this color change by uv–vis spectrophotometry showed that the five-coordinate complex ClFe(Et$_2$dtc)$_2$[6] was being quantitatively formed.[7] This complex was identified by its uv–vis, ir, ^{1}H NMR, and mass spectra. The spectral features given by line f in Figure 1 exactly match those of ClFe(Et$_2$dtc)$_2$ which was independently synthesized.[6]

Time-dependent uv–vis spectra for the photolysis in CHCl$_3$ and C$_6$H$_5$Cl at 265 nm showed good isosbestic behavior (see Figure 1) during the first 90 min and no new bands appeared in the range 650–300 nm other than ones assignable to ClFe(Et$_2$dtc)$_2$. The spectra displayed in Figure 1 show the spectral changes which occur on going from Fe(Et$_2$dtc)$_3$ almost completely into ClFe(Et$_2$dtc)$_2$ (only a spectrophotometrically undetectable amount of Fe(Et$_2$dtc)$_3$ remains after 90 min of photolysis). Further evidence for a stoichiometric reaction is provided by carefully monitoring the progress of the reaction. Disappearance and appearance quantum yields were determined by monitoring spectral changes at 350 and 480 nm, where Fe(Et$_2$dtc)$_2$ and ClFe(Et$_2$dtc)$_2$ predominantly absorb, respectively. Simultaneous equations were solved for concentrations using independently determined extinction coefficients for Fe(Et$_2$dtc)$_3$ and ClFe(Et$_2$dtc)$_2$. Disappearance quantum yields are shown in Table I. The disappearance and appearance quantum yields in CHCl$_3$ and C$_6$H$_5$Cl are identical within experimental error. These numbers were determined and are constant in the range of 0–25% conversion to ClFe(Et$_2$dtc)$_2$.

Table I. Disappearance Quantum Yields for Fe(Et$_2$dtc)$_3$ in CHCl$_3$ and C$_6$H$_5$Cl[a]

Solvent	$\Phi_{265\text{nm}}$	$\Phi_{313\text{nm}}$
CHCl$_3$	0.26	0.15
C$_6$H$_5$Cl	0.39	0.07

[a] Photolysis through quartz in degassed solution at 30 °C; analysis by uv–vis spectral changes (see text). Quantum yields are precise to within ±10%.

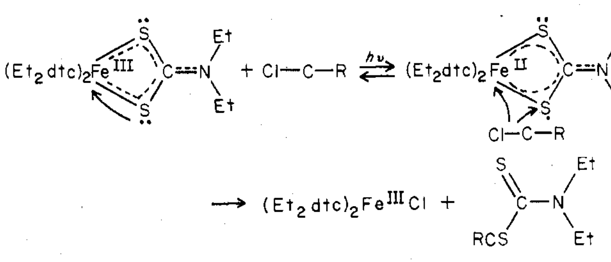
Table II. Uv-Vis Spectral Data for Fe(Et$_2$dtc)$_3$ and Ru(Et$_2$dtc)$_3$ in CHCl$_3$ Solution

Transitions			
λ, nm	ε, l. mol^{-1} cm^{-1}	Assignments[a]	Type
		Fe(Et$_2$dtc)$_3$	
265	47 300	$\pi \rightarrow e_g$ hs	Charge transfer
286	sh	$t_{2g} \rightarrow \pi^*$ ls + hs	Charge transfer
350	11 700	$\pi \rightarrow e_g$ ls	Charge transfer
389	sh	$\pi \rightarrow t_{2g}$ hs	Charge transfer
514	2 660	$e_g \rightarrow \pi^*$ hs	Charge transfer
590	1 850	$\pi \rightarrow t_{2g}$ ls	Charge transfer
		Ru(Et$_2$dtc)$_3$	
240	52 000	$\pi \rightarrow e_g$	Charge transfer
369	11 000	$^2T_{2g} \rightarrow {}^2A_{1g}$	d-d
405	sh	$\pi \rightarrow t_{2g}$	Charge transfer
470	3 200	$t_{2g} \rightarrow \pi^*$	Charge transfer
563	1 800	$^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$	d-d

[a] The band assignments are based on a calculation by Nikolov[8] and the hs and ls notation refers to high-spin and low-spin forms of Fe(Et$_2$dtc)$_3$, respectively. In the calculations octahedral symmetry was assumed.

The quantum yield for conversion into ClFe(Et$_2$dtc)$_2$ is a maximum at 265 nm where Fe(Et$_2$dtc)$_3$ has an intense absorption band which has been assigned as a ligand π to metal e$_g$ (high spin) charge transfer.[8] Table II lists the uv–vis spectral transitions with their proposed assignments.[8] Note that Fe(Et$_2$dtc)$_3$ exists as a mixture of high- and low-spin forms.[9] The quantum yield rapidly drops as the irradiating wavelength is increased and the reaction does not occur significantly above ca. 350 nm.[10] With CHCl$_3$ as a solvent the reaction must occur as a result of metal complex excitation and not solvent photolysis because the irradiating wavelengths being employed ($\gtrsim$265 nm) are higher than the wavelengths where CHCl$_3$ absorbs.[11] The fact that Φ_{313} is greater for CHCl$_3$ than for C$_6$H$_5$Cl probably reflects the greater C–Cl bond energy in C$_6$H$_5$Cl. (Bond energies in kcal/mol for CHCl$_3$[12] and C$_6$H$_5$Cl[13] are 71.5 and 86, respectively.) At this wavelength neither CHCl$_3$ nor C$_6$H$_5$Cl absorbs.[11] The reverse order observed for Φ_{265} results apparently because at this wavelength C$_6$H$_5$Cl also absorbs, producing chlorine radicals which react with Fe(Et$_2$dtc)$_3$ to give ClFe(Et$_2$dtc)$_2$.

The mechanism of eq 2 is proposed for the case where



(2)

solvent photolysis does not occur. The first step is a ligand to metal charge-transfer reaction or photoreduction of the metal. The resulting Fe^{II} complex then abstracts chlorine from the solvent leaving a ·C–R radical which is scavenged by the leaving dtc ligand radical. Support for this mechanism is given by the following observations: (a) the air-unstable Fe^{II} complex $Fe(Et_2dtc)_2$[14] reacts rapidly with degassed $CHCl_3$ at 25 °C in the dark to yield $ClFe(Et_2dtc)_2$; (b) in the reaction with C_6H_5Cl the major nonvolatile organic product is $C_6H_5SC(S)NEt_2$ (vide infra); and (c) only a trace of tetraethylthiuram disulfide is found.

A careful product analysis was carried out for the reaction with C_6H_5Cl using MS and GLC analysis. The reaction was run for 22 h using unfiltered radiation[15] from a 450-W mercury vapor lamp on a degassed 20-ml solution ca. 0.02 M in $Fe(Et_2dtc)_3$. The solution was air cooled and did not exceed a temperature of ca. 30 °C. After photolysis the C_6H_5Cl solvent was removed by vacuum distillation and the resulting residue was thoroughly extracted with petroleum ether. The final residue (after extraction) consisted of $ClFe(Et_2dtc)_2$ and some unreacted $Fe(Et_2dtc)_3$. ^1H NMR and uv–vis spectroscopy showed that the reaction proceeded ca. 70% to completion. The organic residue from the petroleum ether extraction consisted of 39 mol % $C_6H_5SC(S)NEt_2$ and 25 mol % phenyl disulfide. The yields are based on the product $ClFe(Et_2dtc)_2$. Phenyl disulfide is a major photolysis product of $C_6H_5SC(S)NEt_2$, and if it is assumed to come exclusively by secondary photolysis, the primary yield of $C_6H_5SC(S)NEt_2$ is ~89 mol %. In addition to the above products 2-chlorobiphenyl, 4-chlorobiphenyl, and trace amounts of biphenyl and tetraethylthiuram disulfide were also found. The chlorobiphenyls were also produced in similar yield by photolysis of pure C_6H_5Cl under the same conditions of time, light intensity, and temperature and therefore are not considered products of the reaction of interest. In addition, when the photolysis is carried out with 0.023 M chlorobenzene in acetonitrile, the chlorobiphenyls are absent whereas the other products are present.

Continued photolysis of $Fe(Et_2dtc)_3$ solutions in $CHCl_3$ or C_6H_5Cl eventually yielded another iron-containing product which has λ_{max} of 364 and 318 nm. Careful photolysis at 265 nm of degassed solutions of pure $ClFe(Et_2dtc)_2$ which was synthesized by the method of Martin[6] gave a disappearance quantum yield of 0.017 at 30°. Isosbestic points are observed during this reaction which again indicate clean conversion to a single product. The identity of this product is not known at present but its uv–vis spectrum matches that of $FeCl_4^-$.[6] Since this product is formed from $ClFe(Et_2dtc)_2$ at a rate which is ~20 times slower than that of reaction 2, it is unlikely to interfere with the spectral changes in Figure 1 or with the quantum yields reported in Table I. After 90 min, however, the bands due to $FeCl_4^-$ begin to appear.

The band which is most photoactive in $Fe(Et_2dtc)_3$ occurs at 265 nm and is assigned as a ligand to metal $\pi \rightarrow e_g$ charge transfer of the high-spin Fe(III) spin state.[8] Experiments are in progress in which the relative amount of the high-spin state is being varied to see if the rates of reaction at 265 and 350 nm are affected. The 350-nm band is assigned as a ligand to metal $\pi \rightarrow e_g$ charge transfer of the low-spin state.[8] Results of these experiments should test the assignments of Nikolov listed in Table II.[8]

In addition to the photochemical reaction described above, $Fe(Et_2dtc)_3$ and $Ru(Et_2dtc)_3$ complexes can be photoreduced in acetone, dimethylformamide, or cyclohexanone to yield *cis*-$(CO)_2M(Et_2dtc)_2$[17–19] and $(CO)Ru(Et_2dtc)_2$[17] where M = Fe or Ru. Complete conversion into the carbonyl complexes can be achieved. These products were identified by partial isolation using petroleum ether extraction and comparison of ir spectra with those of independently synthesized samples (see Experimental Section). The organic products of these reactions have not yet been identified. As was the case with the chlorine abstraction reaction, photolysis at 265 nm is most effective in producing metal carbonyl products. It is possible that solvent photolysis is important in the mechanism of these reactions. Work is in progress on these and similar reactions with other metal complexes. It is anticipated that the photochemistry of transition metal complexes with sulfur-containing ligands will lead to new metal complexes and will provide new routes to known inorganic and organic compounds.

Experimental Section

$Fe(Et_2dtc)_3$,[3] $ClFe(Et_2dtc)_2$,[6] $Ru(Et_2dtc)_3$,[20] $(CO)Ru(Et_2dtc)_2$,[17] $(CO)_2Ru(Et_2dtc)_2$,[17] and $(CO)_2Fe(Et_2dtc)_2$[18,19] were synthesized by literature methods. The carbonyl stretching frequencies in cm^{-1} (KBr disk) observed for $(CO)_2Fe(Et_2dtc)_2$, $(CO)_2Ru(Et_2dtc)_2$, and $(CO)Ru(Et_2dtc)_2$ are 2017, 1962; 2030, 1963; and 1920, respectively. $CHCl_3$ solvent used in photolysis experiments was purified by distillation from BaO under nitrogen and was passed down a basic alumina column just prior to use. C_6H_5Cl solvent was purified by washing reagent grade C_6H_5Cl with H_2SO_4 and $NaHCO_3$ solutions, drying over anhydrous $MgSO_4$, vacuum distilling into molecular sieves, and passing it down an activated alumina column under an N_2 atmosphere just prior to use. All photolysis experiments were carried out at 30 °C under an N_2 atmosphere using filtered or unfiltered radiation from mercury vapor lamps. Uv–vis spectra were recorded on a Cary Model 14 spectrophotometer with a thermostated cell compartment.

Quantitative photolysis was carried out on degassed freshly distilled $CHCl_3$ or C_6H_5Cl solutions ca. 10^{-4} M in $Fe(Et_2dtc)_3$ held in 1-cm quartz cells using a 100-W Hanovia medium-pressure mercury vapor lamp, Type SH. Interference filters were employed to select nearly monochromatic radiation for quantum yield measurements. The interference filters used to isolate the Hg bands at 265 and 313 nm are Optics Technology filters 270 and 310 which have band maxima, band-pass widths (5% transmittance cutoff), and half-bandwidths of 265, 27, 13 and 310, 50, 24 nm, respectively. The intensitites of the filtered light used to determine the quantum yields were determined by ferrioxalate actinometry[21] and were 1.09×10^{-8} and 1.52×10^{-8} einstein min^{-1} for 265 and 313 nm, respectively.

All identified organic products were characterized by ^1H NMR (Varian XL-100), ir, and mass spectroscopy. High-resolution mass spectroscopy was used to confirm the major products. The spectral properties of all of the major products were compared to independently synthesized samples. Quantitative yields were determined by GLC analysis using a Varian Aerograph Model A 90-P3 gas chromatograph. Retention times and peak areas were calibrated with authentic samples of $C_6H_5SC(S)NEt_2$, $C_6H_5SSC_6H_5$, and 2-chloro- and 4-chlorobiphenyl.

Acknowledgment. This research was supported by Grant GP-37795 from the National Science Foundation, by the Research Corp., and by the University of Minnesota Graduate School. Useful discussions with J. I. Zink are also gratefully acknowledged.

Registry No. $Fe(Et_2dtc)_3$, 13963-59-2; $Ru(Et_2dtc)_3$, 31656-15-2; $CHCl_3$, 67-66-3; C_6H_5Cl, 108-90-7.

References and Notes

(1) (a) Lando Summer Research Fellow, 1975. (b) NSF–URP undergraduate, summer 1975.

(2) (a) J. P. Fackler, Jr., A. Avdeef, and R. G. Fischer, Jr., *J. Am. Chem. Soc.*, **95**, 774 (1973); (b) J. I. Zink, D. Schwendiman, and M. J. Incorvia, Abstracts, 169th National Meeting of the American Chemical Society, Philadelphia, Pa. April 7–11, 1975, No. INOR 143.

(3) M. C. Palazzotto, D. J. Duffy, B. L. Edgar, L. Que, Jr., and L. H. Pignolet, *J. Am. Chem. Soc.*, **95**, 4537 (1973).

(4) M. C. Palazzotto and L. H. Pignolet, *Inorg. Chem.*, **13**, 1781 (1974).

(5) L. H. Pignolet and B. M. Mattson, *J. Chem. Soc., Chem. Commun.*, 49 (1975).

(6) R. L. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967).

(7) During the course of our work this same reaction with $Fe(Bzl_2dtc)_3$ was reported; however, product analysis was not carried out (vide infra) and photolysis was only done at wavelengths ≥350 nm.[2]

(8) G. St. Nikolov, *Inorg. Chim. Acta*, **4**, 610 (1970).

(9) R. L. Martin and A. H. White, *Transition Met. Chem.*, **4**, 113 (1968); R. M. Golding, B. D. Lukeman, and E. Sinn, *J. Chem. Phys.*, **56**, 4147 (1972).

(10) Zink[2] has carefully measured the quantum yield where R = benzyl for the reaction in $CHCl_3$ and C_6H_5Cl at 350 nm: $\Phi_{350} = 0.048$ and 0.008,

respectively. At longer wavelengths the reaction does not occur.
(11) The absorbance of pure $CHCl_3$ in a 1-cm cell at 313 and 265 nm is 0.00 and 0.05, respectively. Since the absorbance of the metal complex is ≫2 at the irradiating frequency, little or no light is being absorbed by the $CHCl_3$ solvent. The absorbance of C_6H_5Cl at 313 nm is 0.04.
(12) P. Goldfinger and G. Martens, *J. Chem. Soc.*, 2220 (1961).
(13) R. T. Morrison and R. N. Boyd, "Organic Chemistry", Allyn and Bacon, Boston, 1970 p 46.
(14) J. P. Fackler, Jr., and D. G. Holah, *Inorg. Nucl. Chem. Lett.*, **2**, 251 (1966).
(15) Attempts were made to carry out this reaction using filtered radiation such that λ >300 nm. The quantum yields are so small in this range that no appreciable product could be isolated, so unfiltered radiation was used. The reaction therefore results from a combination of complex and C_6H_5Cl photolysis.
(16) P. A. McCusker and S. M. S. Kennard, *J. Am. Chem. Soc.*, **81**, 2976 (1959).
(17) J. V. Kingston and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 2709 (1966).
(18) F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **3**, 1398 (1964).
(19) H. Buttner and R. D. Feltham, *Inorg. Chem.*, **11**, 971 (1972).
(20) L. H. Pignolet, *Inorg. Chem.*, **13**, 2051 (1974).
(21) J. C. Calvert and J. N. Pitts, "Photochemistry", John Wiley and Sons, Inc., New York, 1966, pp. 783-786.

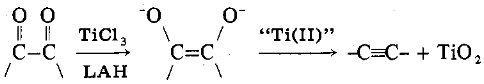
Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

Peroxo-Bridged Titanium(IV)

Dennis P. Bauer and Roger S. Macomber*

Received November 5, 1975 AIC50798P

As part of our search for new synthetic methods of forming carbon–carbon triple bonds, we attempted to extend McMurry's titanium trichloride–lithium aluminum hydride carbonyl coupling reaction[1] to α-diketones

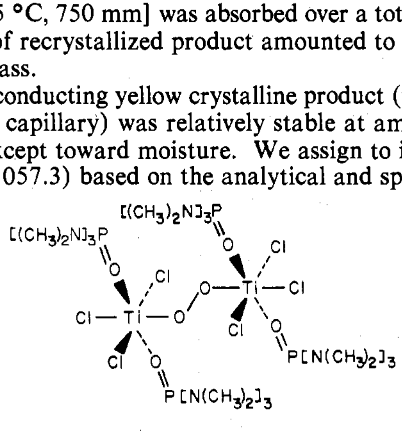


$$\mathrm{O{=}C{-}C{=}O} \xrightarrow[\text{LAH}]{\text{TiCl}_3} {}^{-}\mathrm{O{-}C{=}C{-}O}^{-} \xrightarrow{\text{"Ti(II)"}} \mathrm{-C{\equiv}C-} + \mathrm{TiO_2}$$

A variety of solvents and conditions were examined with little success, but anomalous behavior in hexamethylphosphoramide (HMPA) led us to investigate the reaction of $TiCl_3$ with HMPA.

Titanium trichloride forms a trisolvate with tetrahydrofuran (THF),[2] and there is a terse mention of $TiCl_3{\cdot}HMPA$ and $TiCl_3{\cdot}2HMPA$ (both have mp >360 °C, but no other data were given) in patent literature.[3] We found that reaction of a purple suspension of $TiCl_3$ in THF with 2 mol of HMPA under argon resulted in formation of a turquoise suspension we attribute to $TiCl_3{\cdot}2HMPA$.[4] This suspension was stable under argon, but exposure to air or oxygen caused an immediate color change to yellow and formation of a crystalline solid. When 5.0 mmol of $TiCl_3{\cdot}2HMPA$ in THF was placed in contact with pure oxygen at ca. 1 atm, 55.7 ml [2.25 mmol (90%) at 25 °C, 750 mm] was absorbed over a total of 96 h.[5] The mass of recrystallized product amounted to 90% of the reactant mass.

The nonconducting yellow crystalline product (mp 230 °C dec, sealed capillary) was relatively stable at ambient temperature except toward moisture. We assign to it structure I (mol wt 1057.3) based on the analytical and spectral data given in the Experimental Section. Note that the titanium atoms are now in the +4 oxidation state. Of particular significance are the Raman band at 970 cm^{-1} (O–O stretch[6]), the ir bands at 530, 483 and 1194 cm^{-1} (Ti–O[7a] and O-coordinated P═O[7b]), and the absence of a uv absorption for Ti(III).[7a] The lone doublet in the ^{1}H NMR spectrum of I further suggests that the HMPA molecules are symmetrically arranged at least on the time average at room temperature.



I

When oxygen was admitted to the $TiCl_3{\cdot}3THF$ suspension before HMPA was added, the color slowly (ca. 10 min) changed to light yellow, and a clear solution resulted. After 3 h, HMPA was added and I immediately began to crystallize out.

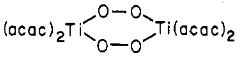
It is important to compare the above behavior to the reactions of other Ti(III) complexes with oxygen. $TiCl_3$ itself is reported[8] to give TiClO, which must involve redox at chlorine as well as oxygen. More interesting is the reaction of $Ti(acac)_3$ with oxygen, which involves a "slow" blue → yellow color change.[9] The product has been assigned structures II,[9a] III,[9b] and IV[9c] mainly on the bases of elemental analyses

$\mathrm{(acac)_3Ti{-}O{-}Ti(acac)_3}$

II

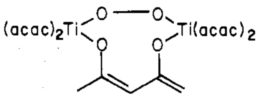
$\mathrm{(acac)_2Ti{=}O}$

III



IV

and infrared data.[9c] [Anal. Calcd for II: C, 51.00; H, 5.99. Calcd for III: C, 45.82; H, 5.38. Found: C, 45.30; H, 5.60. Calcd for IV: C, 43.19; H, 5.07. Found: C, 45.30; H, 7.59.] No oxygen uptake experiments were done. Both III and IV seem to require the oxidation of the acac ligand that is lost. On the basis of our results, we feel this compound may be better formulated as V, where one of the acac ligands bridges



V

both Ti atoms. [Anal. Calcd: C, 48.34; H, 5.51.]

Thus it appears that hexacoordinate Ti(III) is relatively slow to react with oxygen, while the pentaccordinated $TiCl_3{\cdot}2HMPA$[3] reacts readily to form a relatively insoluble peroxo-bridged dimer. Although much work has been done in the general area of peroxy-bridged complexes[10] and at least one peroxo-bridged dimer of Ti(III) is known,[11] compound I seems to be the first example of monoperoxy-bridged titanium(IV).

Experimental Section

Instruments. Beckman IR-12, Varian A-60 (^{1}H), RC-16B2 conductivity bridge, Hitachi RMU-7, Cary 14 (uv), and Spex 1401 Raman (argon laser) instruments were used.

Reagents. HMPA was distilled from sodium; THF, from lithium aluminum hydride. $TiCl_3$ was purchased from Alfa Inorganics.

Preparation of μ-Peroxo-bis[trichlorobis(hexamethylphosphoramide)titanium(IV)]. Titantium trichloride (1.54 g, 10 mmol) and 50 ml of dry degassed THF were combined in a dry flask under argon. The purple suspension was magnetically stirred for 5 min; then 3.58 g (20 mmol) of HMPA was added via syringe. The mixture was stirred for 24 h, during which it became light turquoise; then pure oxygen was bubbled in for 36 h. The color changed to yellow as oxygen was absorbed (see text). Anhydrous ether (50 ml) was added, and the crude yellow solid was isolated by filtration. Recrystallization from dry benzene yielded 4.48 g (85%) of I as yellow needles. An oxidation period of 96 h yielded 90% of I. Anal. Calcd for $C_{24}H_{72}Cl_6N_{12}O_6P_4Ti_2$ (C, H, N, Cl by Chemalytics, Tempe, Ariz.; Ti by the method in "Comprehensive Inorganic Chemistry", Vol. 3, Pergamon Press, Oxford, 1973, p 360): C, 27.26; H, 6.86; N, 15.89; Cl, 20.12; Ti, 9.06. Found: C, 27.06; H, 7.03; N, 15.92; Cl, 21.10; Ti, 9.21. Conductivity is 0.014 Ω^{-1} cm^2 mol in CH_3NO_2.[14]