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 $\lambda > 300$ 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.

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Peroxo-Bridged Titanium(IV)

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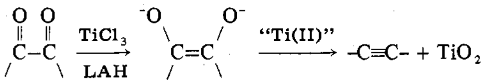
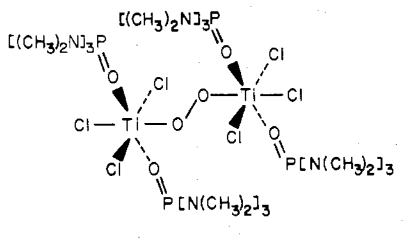
As part of our search for new synthetic methods of forming carbon–carbon triple bonds, we attempted to extend McMurry's titanium trichloride–lithium aluminum hydride carbonyl coupling reaction[1] to α-diketones



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.

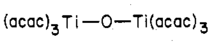
The nonconducting yellow crystalline product (mp 230 °C dec, sealed capillary) was relatively stable at ambient temperature except toward moisture. We assign to it structure I (mol wt 1057.3) based on the analytical and spectral data given in the Experimental Section. Note that the titanium atoms are 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.



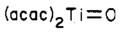
I

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.

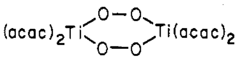
It is important to compare the above behavior to the reactions of other Ti(III) complexes with oxygen. $TiCl_3$ itself is reported[8] to give TiClO, which must involve redox at chlorine as well as oxygen. More interesting is the reaction of $Ti(acac)_3$ with oxygen, which involves a "slow" blue → yellow color change.[9] The product has been assigned structures II,[9a] III,[9b] and IV[9c] mainly on the bases of elemental analyses 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 both Ti atoms. [Anal. Calcd: C, 48.34; H, 5.51.]



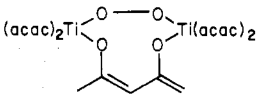
II



III



IV



V

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]

Spectral Data. ^{1}H NMR ($CDCl_3$): δ 2.92 (d, J = 10 Hz).[12] Uv–vis (CH_3NO_2): λ_{max} 372 nm (log ϵ 3.05). Ir ($CHCl_3$, NaCl cells): 2935 (m), 2850 (m), 2810 (w), 1485 (m), 1460 (m), 1305 (m), 1235 (w), 1194 (m), 1128 (s), 1070 (m), 1045 (m), 998 (vs), 970 (sh), 759 (m), 732 (m), 700 (w), 652 (vw) cm^{-1}. Ir (Nujol, polyethylene cells): 530 (m), 483 (s), 380 (sh), 365 (s), 340 (s), 300 (m), 225 (w) cm^{-1}. Raman: 1480 (w), 1445 (w), 1420 (w), 1310 (vw), 1155 (m), 1090 (vw), 1070 (vw), 990 (sh), 970 (vs), 760 (w), 653 (s), 520 (m), 480 (vw), 360 (m), 307 (s), 220 (w, sh) cm^{-1}. Mass spectrum, *m/e* (relative abundance, assignment): 332[13] (4.0, $TiCl_3 \cdot HMPA$), 297[13] (2.5, $TiCl_2 \cdot HMPA$), 188[13] (22, $TiCl_4$), 179 (100, HMPA), 153[13] (37, $TiCl_3$), 135 (95, $O{=}P[N(CH_3)_2]_2$), 92 (63, $O{=}PN(CH_3)_2$), 44 (61, $N(CH_3)_2$).

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Registry No. I, 59219-54-4.

References and Notes

(1) J. E. Mc Murry and M. P. Fleming, *J. Am. Chem. Soc.*, **96**, 4708 (1974), and other papers in the series.
(2) (a) R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, *J. Chem. Soc.*, 379 (1963); (b) G. W. A. Fowles, R. A. Hoodless, and R. A. Walton, *ibid.*, 5873 (1963).
(3) *Chem. Abstr.*, **71**, 39 789, 49 231 (1969). It is likely that, in THF, the sixth coordination site in $TiCl_3 \cdot 2HMPA$ is occupied by a solvent molecule, which is readily displaced by oxygen.
(4) Similar behavior was observed in toluene, the solvent previously used to prepare $TiCl_3 \cdot 2HMPA$.[3]
(5) The uptake rate was initially rapid, with approximately half of the theoretical amount absorbed after 1.5 h.
(6) T. P. Freedman, C. M. Yoshida, and T. M. Leohr, *J. Chem. Soc., Chem. Commun.*, 1016 (1974); A. J. Meleuger, L. R. Anderson, and C. T. Ratcliffe, *Appl. Spectrosc.*, **26**, 381 (1972).
(7) (a) R. S. P. Coutts, P. C. Wailes, and R. L. Martin, *J. Organomet. Chem.*, **50**, 145 (1973); (b) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2**, 572 (1963).
(8) H. Schafer, F. Wartenpfuhl, and W. Weise, *Z. Anorg. Allg. Chem.*, **295**, 268 (1958); N. V. Ageer, *Chem. Abstr.*, **79**, 147 791 (1973).
(9) (a) B. N. Chakravarte, *Naturwissenschaften*, **45**, 286 (1958). (b) M. Cox, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2840 (1965). (c) B. R. McGarvey and E. L. Tepper, *Inorg. Chem.*, **8**, 498 (1969). Cryoscopic molecular weights were somewhat ambiguous. Structure assignment was based on the absence of Ti═O stretch and mass spectral data.
(10) W. P. Griffith, *Coord. Chem. Rev.*, **5**, 459 (1970).
(11) J. J. Salzman, *Helv. Chim. Acta*, **51**, 903 (1968).
(12) The methyl doublet of HMPA occurs at δ 2.66; that of $TlCl_3 \cdot 2HMPA$, at δ 2.83.
(13) Lowest *m/e* peak of chlorine isotope cluster.
(14) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

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Stereochemistry of Chlorine Oxidation of Some Dimethyl Sulfoxide–Cobalt(III) Complexes

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The evidence for intermediates of reduced coordination numbers arising from rapid induced aquation of coordinated ligands in cobalt(III) amine complexes comes from two sources. First, the competition ratios for nucleophiles relative to water (both anions and neutral nucleophiles) were essentially independent of the leaving group.[1] Second, the stereochemistry of the reaction products was also independent of the leaving group.[1]

The induced aquation reactions suitable for yielding the second set of data were limited: namely, the nitrosation of coordinated azide ion,[2] e.g.

$$\begin{aligned}&(en)_2CoClN_3{}^{+} + NO^{+} \rightarrow (en)_2CoCl(NNNNO)^{2+}\\ &\quad\rightarrow (en)_2CoCl^{2+} + N_2 + N_2O\\ &\qquad\downarrow H_2O\\ &\quad(en)_2CoClOH_2{}^{2+}\end{aligned}$$

and the Hg^{2+}-catalyzed aquation of halide ion,[2] e.g.

$$(en)_2CoCl_2{}^{+} + Hg^{2+} \rightarrow (en)_2CoCl^{2+} + HgCl^{+} \xrightarrow{H_2O} (en)_2CoClOH_2{}^{2+}$$

A portion of the data suffers from the problem that two such examples could coincidentally agree and there is an obvious need to generate the intermediate by some other route. This aspect of substitution chemistry is complementary of course to a need for finding more methods of accelerating what are usually relatively slow reactions and to putting the intermediates to use for synthetic purposes.[1]

We report here additional evidence for the five-coordinate $[Co(en)_2X]^{2+}$ intermediates generated by Cl_2 oxidation of dimethyl sulfoxide (DMSO) in *cis*-$[Co(en)_2(DMSO)X]^{n+}$ ions (X = Cl, OH_2, DMSO).

Results and Discussion

Only one isomer of $Co(en)_2(DMSO)Cl^{2+}$ is known[3] and this has been assigned as the cis configuration with DMSO oxygen bonded[3,4] from the amine proton signal pattern in the ^{1}H NMR and from the similarity of its visible spectrum to that of *cis*-$Co(en)_2(OH_2)Cl^{2+}$. This cis configuration is now confirmed, both by the observation of the small (~1 Hz at 100 MHz) diastereotopic splitting in the DMSO methyl resonances in the ^{1}H NMR (10^{-3} M DCl) and by its resolution into catoptric forms (vide infra). The cis assignment for the other DMSO (and TMSO)[5] complexes reported herein follows similarly.

cis-$[Co(en)_2(DMSO)Cl](ClO_4)_2$ or $[Co(en)_2(DMSO)Cl]NO_3ClO_4$ (ϵ_{519} 96.8, H_2O; ϵ_{521} 112.0, DMSO) reacts rapidly (seconds, 20 °C) with excess Cl_2 (0.02–0.08 M) in dilute solution (3×10^{-4} to 10^{-2} M) in aqueous $HClO_4$ (0.01–0.1 M). The visible spectrum after 5 min (ϵ_{510} 70.5 ± 0.8 (5))[6] corresponds to 74 ± 1% *cis*- and 26 ± 1% *trans*-$Co(en)_2(OH_2)Cl^{2+}$. Similar experiments in which excess (200-fold) $NaHCO_3$ was added following oxidation showed ϵ_{510} 107 ± 2 (3) after 5–10 min. Analysis in terms of $Co(en)_2CO_3{}^{+}$ (ϵ_{510} 133.8) and *trans*-$Co(en)_2ClOCO_2(H)^{n+}$ (ϵ_{510} 21.2)[7] revealed an identical isomer composition, 76 ± 2% cis.

(−)-*cis*-$[Co(en)_2(DMSO)Cl](ClO_4)_2$ ($[\alpha]_{589}$ −247°, $[\alpha]_{578}$ −308°, $[\alpha]_{560}$ −324°, $[\alpha]_{480}$ +439°, $[\alpha]_{350}$ +782°, 20 °C, 0.01 M $HClO_4$, c 1.69×10^{-3} g/ml; $[\alpha]_{589}$ −197°, $[\alpha]_{578}$ −191°, $[\alpha]_{510}$ +384°, $[\alpha]_{350}$ +745°, 20 °C, DMSO, c 1.75×10^{-3} g/ml) and (−)-$[Co(en)_2(DMSO)Cl]NO_3ClO_4$ were prepared by allowing (−)-*cis*-$[Co(en)_2Cl_2]ClO_4$ ($[\alpha]_{589}$ −575°)[8] to react with $AgClO_4$ (1.05 equiv) in DMSO (1 h, 20 °C). Work-up by the usual procedure[3] yielded crystals of the diperchlorate which were recrystallized from water to constant rotation. After reaction with Cl_2 in $HClO_4$ (0.01 M) as above the visible and rotary dispersion spectra were recorded (ϵ_{510} 70.5 ± 0.5 (2), $[M]^{20}_{589}$ −715 ± 20 (2)° M^{-1} m^{-1}, $[M]^{20}_{578}$ −935 ± 20 (2)° M^{-1} m^{-1}).[9] The properties recorded[8] for (−)-*cis*-$[Co(en)_2(OH_2)Cl]Br_2 \cdot H_2O$ (ϵ_{510} 91.2, $[M]^{20}_{589}$ −903°, $[M]^{20}_{578}$ −1272°) and *trans*-$[Co(en)_2(OH_2)Cl]SO_4$ (ϵ_{510} 11.0) show that the spectrophotometric data correspond to 74 ± 1% cis, and the polarimetric data, to 76 ± 3% (−)-cis product. The fraction of optically pure cis product was fixed more precisely by quenching with $HCO_3{}^{-}$, as earlier (ϵ_{510} 106.5 ± 1.0 (2), $[M]^{20}_{589}$ −3480 ± 20°, $[M]^{20}_{578}$ −4100 ± 20°, $[M]^{20}_{490}$ +6550 ± 20°). Optically pure (−)-$[Co(en)_2CO_3]ClO_4 \cdot 0.5H_2O$ in this medium shows $[M]^{20}_{589}$ −4590°, $[M]^{20}_{578}$ −5430°,