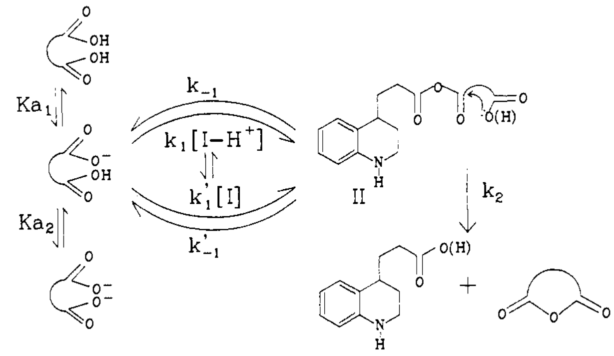
Scheme I[7,8]



stable cyclic anhydrides are ~1-2 orders of magnitude more reactive than acetate, malonate, or *trans*-1,2-cyclopropane dicarboxylic acid at pH 5.0 even after due account of disparities in [ionic species] is taken. In aqueous media (succinate buffers, μ = 0.3 M (KCl) T = 25 °C) succinate exhibits the simplest kinetic behavior. The pH vs. log (k_2^{obsd}) profile from pH 3.5-6.5 exhibits a plateau at low pH indicative of the dominance of the mono anionic form of succinate reacting with protonated I[7] (Table 1S, Supplementary Material). Under these conditions the reaction is driven by the closure of II to form succinic anhydride (k_2 in Scheme I), that process competing effectively with k_{-1} and k_{-1}'.[8] When the FTIR spectrum of 0.1 M I in CH_3CN containing equimolar $Et_3N^+H/O_2^-CCH_2CH_2CO_2H$ is periodically monitored,[9] the characteristic C=O stretches of succinic anhydride (1789 and 1862 cm^{-1}) are seen to grow at the expense of the overlapping C=O bonds of I and succinate. Bands characteristic of the linear anhydride II are not observed. After ~10 h in that medium, an equilibrium is established which, judging by peak intensities, favors succinic anhydride by a factor of ~2. A similar situation exists under the same conditions for glutarate monoanion, and after the establishment of equilibrium, mass spectrometric analysis of the product mixture shows prominent peaks characteristic of the amino acid of I (M^+ = 205). In the above experiments neither succinate (glutarate) alone nor in the presence of the authentic amino acid of I shows a tendency to form anhydrides. Finally, the FTIR spectrum of a CH_3CN solution containing 0.1 M I and equimolar $Et_3N^+H/O_2^-CCH_3$, monitored over a 24-h period, shows no detectable bands characteristic of an anhydride and no loss of I. However CH_3CN solutions containing 0.02 M I and 5 M $Et_3N^+H/O_2^-CCD_3$ produce an approximate 1:1 equilibrium mixture of I and its CD_3^- acetate derived open anhydride judging from ^1H NMR, and UV spectrophotometry. The presence of that anhydride is also verified by CI-MS spectrometry (M^+ = 251, $C_{14}H_{14}D_3NO_3 + H^+$). Importantly, when a 25-μL aliquot of the above solution is directly injected into 3 mL of an aqueous, pH 4.75, 0.3 M acetate buffered medium, an immediate regeneration of I is observed, along with its subsequent normal hydrolysis to the amino acid.[10] Hence k_{-1} in Scheme I must be much larger than $k_1[O^-Ac]$ so that nucleophilic attack of carboxylate alone cannot lead to significant hydrolysis of I in the absence of a suitably oriented second intramolecular carboxyl group.[11]

Table I. Second-Order Rate Constants for Attack of Various Acids on Amide I[a]

acid	% monoanion	$k_2^{\text{obsd}\,c}$ ($\times 10^3$ M^{-1} s^{-1})
acetic	74	2.0
succinic	60	250
glutaric	46	172
cis-cyclopropane-1,2-dicarboxylic[b]	85	114
trans-cyclopropane-1,2-dicarboxylic	27	3.1
malonic	55	2.3

[a] T = 25.0 °C, μ = 0.3 M (KCl), pH 5.0 (pK_a values at μ = 0.3 M given in Supplementary Material). [b] pH 5.05. [c] Error limits ±2% of value or better.

The striking feature of the process is a hydrolysis of I without water per se, since the latter's constituents are created stepwise by the conversion of a diacid into a cyclic anhydride. In this case, the driving force for the process obtains from the unique torsional destabilization of I.[6b] Interestingly, substrate distortion has been considered[12] as an important component for catalysis in the APases. While one cannot be certain this model is an accurate reflection of the enzymatic pathway, phenomenologically, the observation of amide hydrolysis promoted by diacids bears a relationship to the situation in the APases and merits continued investigation.

Acknowledgment. We gratefully acknowledge the financial assistances of the University of Alberta and Natural Sciences and Engineering Research Council of Canada as well as Jim Hoyle for technical assistance and Dr. Paul Street (University of Houston) for preliminary observations in this system.

Supplementary Material Available: Tables of kinetic data for succinate with I and pK_a values of various acids titrated at μ = 0.3 M (1 page). Ordering information is given on any current masthead page.

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(7) UV kinetic procedures ar analogous to those reported for the hydrolysis of I.[6a,b] Second-order rate constants for succinate attack on I (k_2^{obsd}) were determined from the slopes of the pseudo-first-order rate constant, k_{obsd} vs. [succinate]$_t$ at various pH values with [succinate]$_t$ = 0.01-0.10 M. The experimental data are given as Supplementary Material. The fit of the kinetic data to Scheme I involving only I-H$^+$ and monoanion is unsatisfactory at higher pH. However, the fit is markedly improved by the inclusion of a term corresponding to the monoanion attacking I or its kinetic equivalent. This latter process is included in scheme I for completeness.

(8) Scheme I is highly simplified since it does not explicitly consider tetrahedral intermediates, and there are kinetically equivalent pathways which at this time cannot be distinguished (e.g., dianion of succinate + I-H$^+$ is equivalent to monoanion + I). Also II, being a dibasic acid has four pH dependent forms. The k_{-1} and k_2 terms will be, respectively, suppressed when the amino and CO_2^- groups of II are protonated.

(9) FTIR spectra recorded in 0.1-mm cell every 10 min over a 16-h period.

(10) Hydrolysis k_{obsd} for I formed by reclosure = 1.64×10^{-3} s^{-1} while k_{obsd} for authentic I = 1.70×10^{-3} s^{-1} under identical conditions, pH 4.75, 0.3 M acetate, T = 25 °C.

(11) The modest catalysis seen with acetate arises from general acid/base promotion of H_2O attack.[6a]

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Titanium-Activated Carbon-Carbon Bond Formation by Reductive Head-to-Head Coupling of Carbon Disulfide: Synthesis of $[(\eta^5\text{-}C_5H_5)_2Ti]_2(C_2S_4)$ and Comparative Analysis of This Electron-Delocalized Tetrathiolene-Bridged Dititanium Complex with the Electronically Equivalent, Electron-Localized Oxalate- and Tetra-*p*-tolyloxalylamidine-Bridged Dititanium Complexes

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Metal-promoted reductive fixation of carbon disulfide to form the tetrathiooxalate (or ethylenetetrathiolate) anion has received much attention in recent years, partly due to problems encountered in obtaining tetrathiooxalate salts by electrochemical dimerization of CS_2.[2] Interest in developing new transition-metal tetrathio-

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(1) On leave (Sept 1983-Feb 1984) from the School of Chemistry, University of New South Wales, Kensington, New South Wales 2033, Australia.

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oxalate complexes and in understanding their structural and electronic relationships is also motivated by their possible use in syntheses of extended one- and two-dimensional metal tetrathiolene arrays with metallic or semiconducting properties.[3]

Prior to this report, all metal-activated reductive head-to-head dimerizations of CS_2 to give C_2S_4-bridged ligands have involved the use of *late* transiton metals. In 1982 Johnson, Lewis, and co-workers[4] described the isolation and structural determination of $[Fe_2(CO)_6]_2(C_2S_4)$ in which two $Fe_2(CO)_6$ moieties are each attached by both iron atoms to each of two thiolate groups of an ethylenetetrathiolate-like C_2S_4 ligand in an end-on bis(1,1′-dithiocarbamate-type) chelation. In the same year we reported the high yield synthesis and structural–electrochemical analysis of $[(\eta^5\text{-}C_5Me_5)Ni]_2(C_2S_4)$, the first example of a π-delocalized bis(1,2-dithiolene) C_2S_4-bridged dimetal complex.[5] This investigation led to the synthesis and structural determinations of $[(\eta^5\text{-}C_5Me_5)Co]_2(C_2S_4)$ and *trans*-$[(\eta^5\text{-}C_5Me_5)Fe(CO)]_2(C_2S_4)$; the geometrical variations among these tetrathiolene-like dimetal complexes were found to be consistent with Fenske–Hall-type MO calculations.[6] An extensive experimental and theoretical study of highly electroactive C_2S_4- and C_2Se_4-bridged dimetal dications of formula $[((triphos)M)_2(C_2X_4)]^{2+}$ (where M = Rh, X = S, Se; M = Ir, X = S; triphos = $MeC(CH_2PPh_2)_3$) was carried out by Bianchini et al.;[7-9] the genesis of the C_2S_4-bridged ligand from two dihapto-coordinated CS_2 ligands was theoretically analyzed.[9] As part of a comprehensive theoretical examination of observed dimeric and possible polymeric stacking patterns in transition-metal bisdithiolenes and tetrathiolates, Hoffmann and co-workers[3] performed MO calculations on both end-on and side-on chelate linkages of metal fragments with C_2S_4-bridged ligands.

We now report that reductive head-to-head dimerization of CS_2 can also be achieved via activation with an *early* transition metal. The reaction of $Ti(\eta^5\text{-}C_5H_5)_2(CO)_2$ with neat CS_2 gives rise to the sought-after $[Ti(\eta^5\text{-}C_5H_5)_2]_2(C_2S_4)$ (**1**) in high yield. A comparison (presented herein) of the sharply contrasting magnetic, electrochemical, and geometrical features of **1** vs. those of the electronically equivalent oxalate-bridged $[(\eta^5\text{-}C_5H_5)_2Ti]_2(C_2O_4)$ (**2**) [10,11] and tetra-*p*-tolyloxalylamidine-bridged $[(\eta^5\text{-}C_5H_5)_2Ti]_2(C_2(NR)_4)$ (where R = *p*-MeC_6H_4) (*3*)[12] provides convincing evidence that, whereas **2** and **3** possess electron-localized configurations involving the interaction of a $C_2O_4^{2-}$ or $C_2(NR)_4^{2-}$ dianion with two d^1 Ti(III) $(C_5H_5)_2Ti^+$ moieties, **1** has an electron-delocalized configuration which is intermediate (from a valence bond viewpoint) between a tetrathiooxalate $C_2S_4^{2-}$ dianion and an ethylenetetrathiolate $C_2S_4^{4-}$ tetraanion interacting with two d^0 Ti(IV) $(C_5H_5)_2Ti^{2+}$ moieties.

A typical preparation of **1** involved the reaction of $Ti(\eta^5\text{-}C_5H_5)_2(CO)_2$ (1.0 g) in 75 mL of CS_2 solution which was stirred under N_2 at room temperature. The reaction was monitored via IR spectra which revealed the disappearance of the terminal carbonyl frequencies of the starting material after 18–24 h. The resulting residue was separated by filtration from the CS_2 solution, washed with hexane, and extracted with CH_2Cl_2 to give the desired dark purple product **1** in 80% yield. This compound was characterized by spectroscopic, magnetic susceptibility, and electrochemical measurements;[13,14] its identity was established from mass spectral data[13] and substantiated by an X-ray crystallographic study.[15,16]

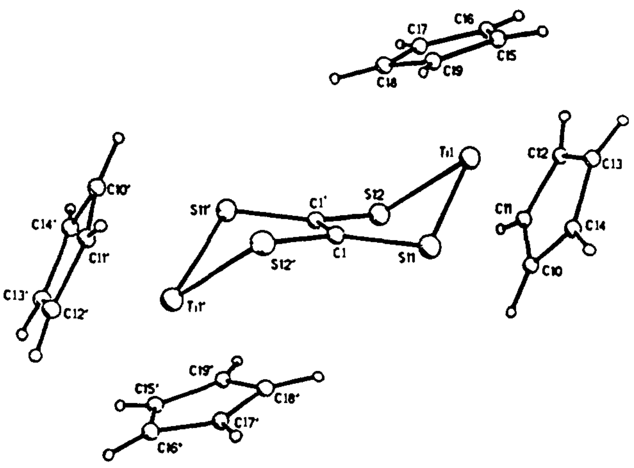

Figure 1. View of $[(\eta^5\text{-}C_5H_5)_2Ti]_2(C_2S_4)$ (**1**) which has crystallographic C_i-$\bar{1}$ site symmetry and pseudo C_{2h}-$2/m$ symmetry. The four crystallographically independent half molecules of **1** possess virtually identical configurations. The bridging C_2S_4 ligand is coordinated to the two equivalent $Ti(C_5H_5)_2$ moieties in a bis(1,2-dithiolene-like) fashion to give two fused, nonplanar TiS_2C_2 rings which are trans-folded along the S···S lines by 46°. Pertinent mean distances for the four half molecules are: Ti–S, 2.414 Å; C–S, 1.736 Å; C–C, 1.41 Å; S1···S2, 3.170 Å; S1···S2′, 2.994 Å.

Initial reactions of $Ti(\eta^5\text{-}C_5H_5)_2(CO)_2$ with CS_2 in benzene produced **1** in much smaller yields (<40%) along with a green complex which was ascertained from a ^1H NMR spectrum and an X-ray crystallographic determination to be $(\eta^5\text{-}C_5H_5)_2Ti(S_2C_2H_2)$ (**4**). this monotitanium dithiolene product, which was previously synthesized[17] by the reaction of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ with $Na_2S_2C_2H_2$ and structurally characterized,[18a] must likewise have evolved in our preparation from a metal-assisted head-to-head reductive dimerization of CS_2.

The magnetic and electrochemical properties of the C_2S_4-bridged **1** markedly differ from those of the C_2O_4-bridged **2** and $C_2(NR)_4$-bridged **3**. That **1** is diamagnetic was shown at room temperature from a solid-state magnetic susceptibility measurement[13] in accordance with its relatively sharp ^1H NMR signal and the absence of any observable EPR signal in solution at room

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(13) $[(\eta^5\text{-}C_5H_5)_2Ti]_2(C_2S_4)$, **1**: IR ($CH_2Cl_2$), no characteristic bands within 1600–3000 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.96; UV–vis (CH_2Cl_2), λ (nm) 837.2 (ϵ 7200), 561 (ϵ 1400), 484 (ϵ 3400), 313 (ϵ 20000). A mass spectrum (electron impact, 12 eV) exhibited the parent ion peak for which a peak match was obtained (*m*/*e* 507.9448; esd 1×10^{-4}). A solid-state magnetic susceptibility measurement at room temperature via a TME balance conclusively showed this compound to be diamagnetic ($\chi_g = -0.32 \times 10^{-6}$ cgs units, 22 °C).

(14) A CV of **1** in THF/0.1 M $[NBu_4]^+[PF_6]^-$ at a Pt disk electrode with a scan rate of 200 mV/s exhibited two reversible one-electron reductions (vs. SCE) at $E_{1/2} = -0.995$ V ($\Delta E_p = 74$ mV) and $E_{1/2} = -1.72$ V ($\Delta E_p = 80$ mV).

(15) $[(\eta^5\text{-}C_5H_5)_2Ti]_2(C_2S_4)$ (fw, 508.46): black parallelepiped-shaped crystals; triclinic, $P\bar{1}$ (C_i^1-no. 2); $a = 17.582$ (3) Å, $b = 8.156$ (1) Å, $c = 16.743$ (3) Å, $\alpha = 80.70$ (1)°, $\beta = 62.50$ (1)°, $\gamma = 84.67$ (1)°, $V = 2101.1$ (6) Å^3; $p_c = 1.608$ g/cm^3 for $Z = 4$. Least-squares refinement (RAELS[16]) of 3442 independent diffractometry data ($I(hkl) > 3\sigma(I(hkl))$) collected at −145 °C with Mo Kα radiation converged at $R_1(F) = 4.33\%$, $R_2(F) = 6.29\%$.

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temperature or in a THF glass at −105 °C. In contrast, both **2** and **3** are paramagnetic;[11,12] the effective magnetic moment per titanium corresponding to a spin-only value at room temperature is completely consistent with the magnetic separation of two d^1 Ti(III) $Ti(C_5H_5)_2$ fragments by a tetradentate $C_2X_4^{2-}$ ligand (X = O, NR) such that the singlet–triplet energy gap must be small (i.e., weak antiferromagnetic coupling[11]). A cyclic voltammogram of **1** in either CH_2Cl_2 or THF displays two reversible one-electron reductions and no oxidations,[14] whereas both **2** and **3** can be oxidized to their dications. A reasonable interpretation of these electrochemical data is that oxidation to give the d^0 Ti(IV) dications occurs in **2** and **3** (but not in **1**) because the removed electrons are predominantly metal-localized in **2** and **3** (and hence in more energy-destabilized HOMO's).

The four dititanium tetrathiolene-bridged molecules in **1** per unit cell lying on crystallographic inversion centers possess analogous solid-state geometries with the bridging C_2S_4 ligand coordinated to the two centrosymmetrically equivalent $Ti(C_5H_5)_2$ moieties via side-on, 1,2-dithio-chelating C_2S_2 ring linkages (Figure 1). Although the C_2S_4 part of the central $TiS_2C_2S_2Ti$ fragment corresponds within experimental error to a planar D_{2h}–$2/m2/m2/m$ configuration, inclusion of the titanium atoms lowers the pseudo symmetry to C_{2h}–$2/m$ because each of the two TiS_2 planes is inclined by 46° with respect to the $S_2C_2S_2$ plane. This angle of trans folding in **1** is remarkably similar to the observed folding (of 43–46° range) of the TiS_2 plane from the dithiolene S_2C_2 plane about the S···S line in four structurally characterized dicyclopentadienyltitanium dithiolene complexes.[18] This common structural feature implies that the degree of electron delocalization of each TiS_2C_2 ring in the dititanium tetrathiolene complex **1** is similar to that in each of the monotitanium dithiolene complexes.

Major variations between the molecular geometry of **1** and those of $\mathbf{2}^{10}$ and $\mathbf{3}^{12}$ directly point to much greater electron delocalization of the C_2X_4-bridged ligand in **1**. The C–C distances of 1.54 (1) Å in **2** and 1.504 (6) Å in **3** approximately conform to single-bond values in harmony with the C_2X_4-bridged ligand (with X = O, NR) being formulated as a dianion. As electron density is donated by the metal centers onto the C_2X_4 ligand one would expect the C–C bond length to decrease with the limit of charge-transfer corresponding to a $C_2X_4^{4-}$ tetraanion which formally contains a C–C double bond. The average C–C distance (mean, 1.41 Å; 1.40 (2)–1.42 (2) range for four independent half molecules) in **1** suggests (from a valence-bond formalism) that the C_2S_4 ligand in **1** is in an intermediate oxidation state between the dianion and tetraanion. In other words, the tetrathiooxalate ligand is a much better acceptor of electron density and thus can be regarded as a tetrathiolene-like ligand. Another salient structural difference which supports this view is that the tilt of each of the two TiX_2 planes out of the C_2X_4 plane is only 11° for both $\mathbf{2}^{10}$ and $\mathbf{3}^{12}$ compared to 46° for **1**. The considerably larger folding angle in **1** is readily attributed to the much better overlap (and hence much greater molecular stability by electron delocalization) achieved in the HOMO between the titanium $3d_{z^2}$ and $d_{x^2-y^2}$ AO's[19] and the π-acceptor $2b_u$ C_2X_4 orbital for X = S (i.e., for a folding angle of 0°, the resulting titanium–C_2X_4 orbital overlap in the HOMO is zero).

Current studies include completion of theoretical MO calculations on **1**, **2**, and **4** with the nonparameterized Fenske–Hall model,[20] attempted isolation of the monoanion of **1** for a comparative structural-bonding analysis, and possible transfer reactions of the C_2S_4 ligand of **1** to other metals.

Acknowledgment. This research was supported by the National Science Foundation. We are particularly grateful to Dr. R. B. Cody (Nicolet Analytical Instruments) for obtaining a mass spectrum of **1** with a Nicolet FT-MS 1000 mass spectrometer. Special thanks are also due to Professor Brock Spencer (Beloit College) for his help in carrying out the EPR measurements.

Supplementary Material Available: Tables listing the atomic parameters and intramolecular distances and bond angles for $[(\eta^5\text{-}C_5H_5)_2Ti]_2(C_2S_4)$ (**1**) (6 pages); table listing the observed and calculated structure factor amplitudes for **1** (21 pages). Ordering information is given on any current masthead page.

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Conventional and Laser-Jet Photochemistry of 2-Methylbenzophenone[1]

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The current interest in high-intensity laser photochemistry in solution[2] has prompted us to construct a laser-jet photochemical apparatus with which it becomes possible to conduct multiple photon reactions in solution on a substantially enhanced scale. By use of this laser-jet apparatus, the solution to be irradiated is ejected at high velocity from a capillary nozzle (diameter = 100 μm) into the focal region of an argon ion laser. This irradiation configuration allows one to achieve useful CW fluences in the range of 10^{22}–10^{23} photons·cm^{-2}·s^{-1} (3 W, 333–364 nm laser lines). At these intensity levels it should be possible to obtain isolable quantities of photoproducts from absorbing transients having lifetimes as short as about 100 ns.[3]

In this initial work, we have applied the laser-jet technique to the previously studied 2-methylbenzophenone (**1**) system.[4] This system provides (1) a readily accessible target intermediate, the photoenol **E-2** (Scheme I), with a lifetime in the range of several seconds; (2) only one other suitably long-lived intermediate, **3**, which might efficiently absorb a second photon under jet conditions;[5] and (3) a known, albeit very inefficient, photocyclization of **E-2** to the dihydroanthrone tautomer **3**, which ultimately is oxidized to anthrone (**4**).[6] Furthermore, under low-intensity conditions, the *E*- and *Z*-photoenols were though to revert almost exclusively to the starting ketone **1**.

Therefore, during low-intensity control studies, we were surprised to observe that **1** afforded a rather complex mixture of products (Scheme II and Table I).[7] Products **7–11** have never before been reported from this parent photoenol system.[8] The

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(1) Presented at the XI IUPAC Symposium on Photochemistry, Lisbon, Portugal, July 21–Aug 1, 1986.

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(3) To date this laser-jet apparatus has been used to successfully reproduce the extraordinary photochemistry of 1,1,5,5-tetraphenyl-1,5-pentanediyl (τ = 900 ns) first reported by Johnston and Scaiano (ref 2f; we thank Dr. Scaiano for his assistance in repeating this work) as well as to initiate the photochemistry of other shorter lived biradicals. The details of this work was well as a full description of the laser-jet apparatus will be reported in a full paper at a later date.

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(7) The structures of all products were consistent with their spectral properties: *d,l*-**5**, mp 154–155 °C; *meso*-**5**, mp 140–141 °C; **6**, mp 89–91 °C; **8**, mp 162–165 °C; **9**, mp 140–141 °C; **10**, mp 106–107 °C; **11**, mp 120–130 °C dec.

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