complexes, the rate of dimer formation increases in going from X = Cl to I, presumably for steric reasons.[29b] The dimers form more quickly in ethanol than in noncoordinating solvents, such as dichloromethane or benzene.[29b] A similar loss of $P(t\text{-}Bu)_2(\overline{CHCH_2CH_2})$ from 1 in toluene/acetic acid or dioxane must lead to formation of 4. Oxidation of free phosphine to phosphine oxide hinders the reverse reaction.[29a]

Under various conditions complex 1 forms the less sterically congested complexes 2, 3, and 4. However, complex 1 fails to form an internally metalated σ-cyclopropyl complex even though such a complex would be less sterically congested than 1 (Scheme II).

We have previously reported the intramolecular activation of the cyclopropyl ring of the phosphine ligand by the Pt center in *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})_2$ to form a σ-allyl complex.[21a] In this complex the cyclopropyl group is accessible to the Pt atom. In the structures of the present complexes 1–4, the cyclopropyl rings are well removed from the Pt center. Thus, geometric constraints may prevent precoordination of the cyclopropane group to the Pt atom that would encourage cleavage of the strong cyclopropyl C–H bond. If no electronic interactions occur between Pt and cyclopropane in 1 in solution, then a *t*-Bu C–H bond (91.0 kcal/mol) should be more reactive than a cyclopropyl C–H bond (~101 kcal/mol),[30] in agreement with the reaction chemistry found here. Whether activation of this type is thermodynamically or kinetically controlled is not known.[1b]

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Registry No. 1, 107202-80-2; 2, 107202-81-3; 3, 107202-82-4; 4, 107202-83-5; K_2PtCl_4, 10025-99-7; di-*tert*-butylcyclopropylphosphine, 107245-36-3; cyclopropyl bromide, 4333-56-6; di-*tert*-butylchlorophosphine, 13716-10-4.

Supplementary Material Available: Anisotropic thermal parameters (Table IV) and hydrogen atom positions (Table V) (10 pages); structure amplitudes (Table VI) (68 pages). Ordering information is given on any current masthead page.

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Photorearrangements of CuCl Complexes of 1,5,9-Cyclododecatrienes: Wavelength Dependence

Yuan L. Chow,* Xian-en Cheng, and Gonzalo E. Buono-Core

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

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Irradiation of the CuCl complexes of the cis–trans isomers of 1,5,9-cyclododecatriene (CDT) in the presence of an excess of these ligands at wavelength >290 nm caused sequential interconversions of all the possible isomers: *ttt*-CDT $\rightleftarrows$ *ctt*-CDT $\rightleftharpoons$ *cct*-CDT $\rightleftarrows$ *ccc*-CDT. Irradiation of similar solutions at wavelength >240 nm induced irreversible rearrangement of CDT to 9-vinyl-*cis,cis*-1,5-cyclodecadiene (VCDD) in addition to the reversible cis–trans photoisomerizations. The rearrangement was most likely caused by photoexcitation of CuCl·*ccc*-CDT with the light energy corresponding to 240–290 nm, and its mechanisms are proposed.

Introduction

Chemical reactions caused by sensitized, and less frequently direct, excitations of nonconjugated cyclic polyenes have attracted extensive investigations and are known to involve cis–trans isomerization, cycloaddition, and other assorted rearrangements.[1] Nonconjugated polyenes are known to form π-complexes with copper(I) salts;[2,3] the structure and bonding of some of these Cu(I) complexes are well-defined.[2] Owing to the tendency of coordination, photocatalyzed cycloadditions and rearrangements of such polyenes in the presence of Cu(I) salts have been extensively investigated;[4,8] an excellent review on these subjects has been published.[14] Recently we have provided evidence of the isomerization and cycloaddition of 1,5-cyclooctadienes (1,5-COD) complexed with copper(I) salts and, further, a wavelength dependence of these photoreactions in the Cu(I) complexes.[8] This work led us to examine similar CuCl complexes of readily available *trans,trans,-trans*-1,5,9-cyclododecatriene (*ttt*-CDT) and *cis,trans,-trans*-1,5,9-cyclododecatriene (*ctt*-CDT); their photorearrangements are described here.

Sensitized photorearrangements of CDT's have been investigated occasionally in the past.[9-11] The major pathway is the cis–trans isomerization of the olefinic bonds to give a mixture of all possible isomers, e.g., photolysis of *ctt*-CDT to *ttt*-CDT, *cct*-CDT, and *ccc*-CDT, although the disagreement on the presence of the last isomer has

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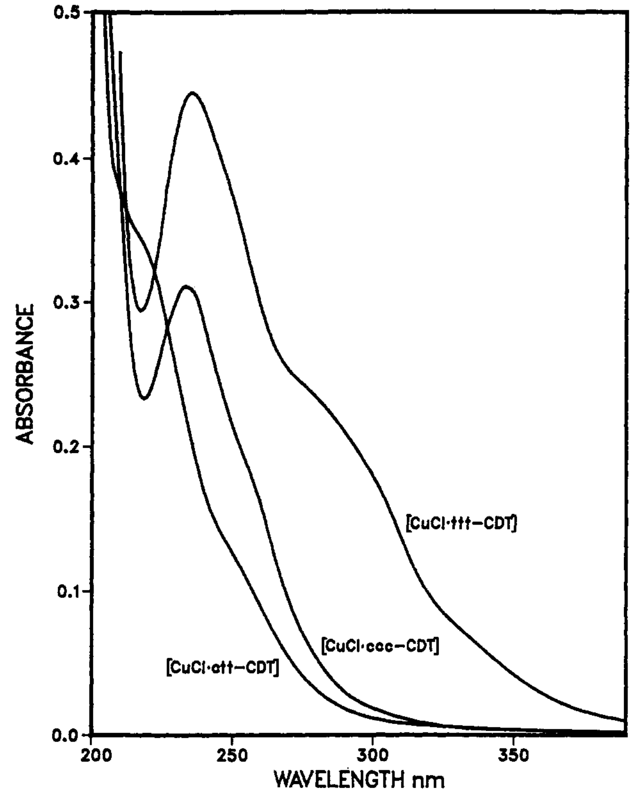
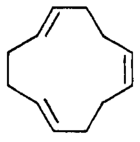
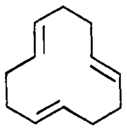


Figure 1. The UV absorption spectra of (a) CuCl·*ttt*-CDT (0.87 mM), (b) CuCl·*ctt*-CDT (0.91 mM), and (c) CuCl·*ccc*-CDT (1.07 mM) in methanol.

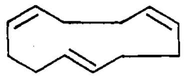
not been resolved.[9,10] In addition, small amounts of the two isomers of **1** are obtained in a direct photolysis,[11] and **2** was also obtained in benzene-sensitized photolysis.[10]



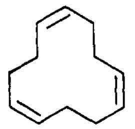
ctt-CDT



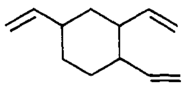
ttt-CDT



cct-CDT



ccc-CDT



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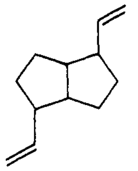

2

Results and Discussion

The cuprous chloride complexes of three available CDT's were prepared according to the published method,[3] and authentic *ccc*-CDT was prepared by the known method.[2,12] The UV absorption spectra of these three CuCl·CDT complexes in methanol (Figure 1) showed tailings above 300 nm. A methonolic solution of CuCl·*ttt*-CDT containing excess *ctt*-CDT was irradiated through a Pyrex filter (cutoff < 290 mm) under nitrogen, and the percent yields of CDT were analyzed by GC. During photolysis copper metal precipitated, but very slowly, and did not retard the reaction significantly. In this and other experiments the recovery of the CDT fraction was >95% confirmed by GC analysis and/or isolation of the products. The GC peaks of these CDT's were assigned by coinjections of authentic samples. The fourth GC peak in the order of elution was due to a mixture of *cct*-CDT and *ccc*-CDT and could be resolved to a barely separated twin peak at a lower temperature; the peak at the lower retention time was confirmed to be the *ccc*-CDT by coinjection with an authentic *ccc*-CDT sample. A semipure sample of *cct*-CDT (78%) was isolated as a mixture with *ccc*-CDT. A photostationary state was obtained in about 10 h (Figure 2), and after 80 h of irradiation only 1.5% of a new product, in addition to CDT peaks, was registered in GC.

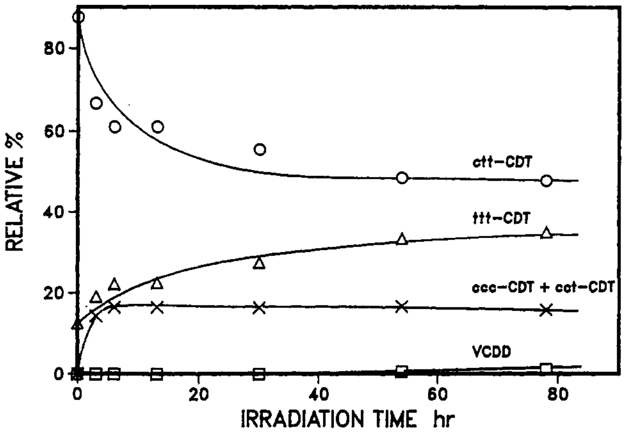

Figure 2. Photolysis of a methanol solution of CuCl·*ttt*-CDT (3.83 mM) and *ctt*-CDT (23.1 mM) through a Pyrex filter.

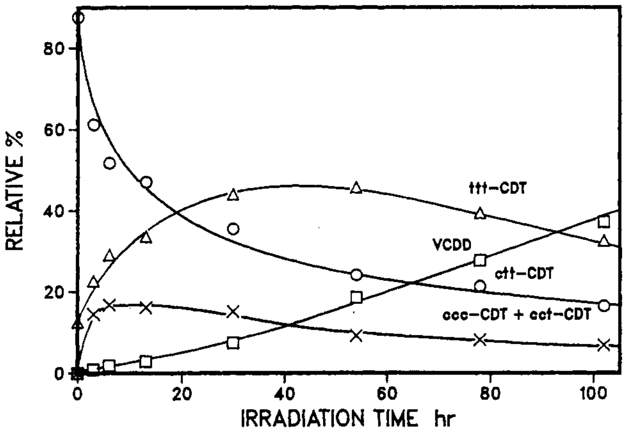

Figure 3. Photolysis of a methanol solution of CuCl·*ttt*-CDT (3.83 mM) and *ctt*-CDT (23.1 mM) through a Corex filter.

Similar photolysis through a Corex filter and GC analysis showed a slow formation of the new product (Figure 3). This photoreaction (Corex filter, cutoff < 240 mm) was retarded by the formation of copper metal film that had to be removed from time to time. The percentage of *ccc*-CDT and *cct*-CDT mixture peaked rapidly in several hours but maintained low concentrations afterward: percentages of *ttt*-CDT were relatively high. These suggested that either *cct*-CDT or *ccc*-CDT was the precursor to the new product that was eventually determined to be 9-vinyl-*cis*,*cis*-1,5-cyclodecadiene (VCDD) by the following evidence.

VCDD became a hard resin slowly when exposed in the air for several weeks but was stable when kept under nitrogen and in a freezer. VCDD absorbs 3 mol of hydrogen to give an ethyl group as shown by a typical CH_3 triplet and a CH_2 double quartet in the NMR spectrum of the hydrogenated product. This proved the presence in VCDD of a vinyl group that was also indicated by the NMR spectrum of VCDD. The remaining two double bonds were endocyclic and had cis configuration as indicated by FT-IR absorption at 709.77 and 735.80 cm^{-1}. This assignment is supported by the similar absorptions of the cis double bonds of model compounds[13,14] shown:

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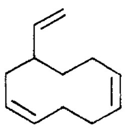
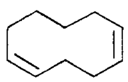
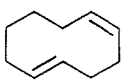
[12] Untch, K. G.; Martin, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 3518.



VCDD



700 cm^{-1} (s)[13]
708 cm^{-1} (s)[14]



960 (m) and 685 cm^{-1} (m)[13]

it is instructive to note that VCDD does not show an absorption typical of a trans configuration at about 960 cm^{-1}. The NMR coupling constant of the two sets of the olefinic protons were both 11.0 Hz and could not be used to indicate the configuration unambiguously. The mass spectrum and ^{13}C NMR spectrum showed that VCDD was an isomer of CDT. Since VCDD contained one vinyl group in addition to two endocyclic double bonds but no methyl group in its NMR spectrum, it must possess a cyclodecane ring. As decoupling experiment showed the presence of only two nonallylic protons, VCDD must have the double bonds in the 1,5 relation as shown.

With silver (trifluoromethyl)sulfate VCDD formed two complexes with the formulas [VCDD·$(AgO_3SCF_3)_3$] and [VCDD·AgO_3SCF_3]. The recrystallized complexes could by crystals but were shown to be microcrystalline from the diffraction pattern and could not be analyzed by X-ray crystallography.

The following reaction scheme can be suggested for the photorearrangements. The metathesis of various CDT ligands in the complexes undoubtedly occurs, and the extent of such reactions depends on the stabilities of the complexes and concentrations of the ligands; they are omitted as equilibria are unknown.

$$\text{CuCl·}ttt\text{-CDT} \overset{h\nu}{\rightleftharpoons} \text{CuCl·}ctt\text{-CDT} \overset{h\nu}{\rightleftharpoons} \text{CuCl·}cct\text{-CDT} \overset{h\nu}{\rightleftharpoons} \text{CuCl·}ccc\text{-CDT} \quad (1)$$

$$\text{CuCl·}ccc\text{-CDT} \xrightarrow[\text{CDT}]{300\text{–}260\text{ nm}} \text{CuCl·CDT} + \text{VCDD} \quad (2)$$

It is clear that a light energy > 290 nm only promotes the cis–trans isomerization of the double bond (reaction 1). The deep-seated rearrangement to VCDD (reaction 2) is promoted by a higher energy source (e.g., 290–240 nm); this wavelength dependence is similar to the photorearrangement of the CuCl complex of *cc*-1,5-COD to tricyclooctane (TCO) as demonstrated before.[8] The immediate precursor of VCDD is most likely CuCl·*ccc*-CDT, but the possibility of CuCl·*cct*-CDT could not be ruled out completely because of unavailability of *cct*-CDT. These proposals are further supported by the following experiments.

Irradiation of respective methanol solutions of CuCl·*ttt*-CDT and CuCl·*ctt*-CDT, whether alone or in the presence of their corresponding ligands, through a Corex filter gave VCDD slowly with an induction period of 10–20 min under the conditions used; the latter case formed VCDD slightly faster and showed very rapid increases of the GC peak of *cct*-CDT + *ccc*-CDT (Figures 4 and 5). Irradiation of CuCl·*ccc*-CDT alone in methanol under similar conditions promptly gave VCDD without an induction period (Figure 5) which supported the above argument. In the absence of ligand such as this experiment and those of above, the copper metal started to deposit rapidly in 15 min and much faster in the case of CuCl·*ccc*-CDT photolysis than those of the other complexes.

Both isomerization and rearrangement were retarded in the presence of acetone, benzene, phenol, or *p*-xylene as sensitizers in the photoreaction. Similar reactions carried out at 77 K retarded the formation of VCDD but promoted the formations of *cct*-CDT and *ccc*-CDT much more rapidly than those experiments carried out at room temperature.

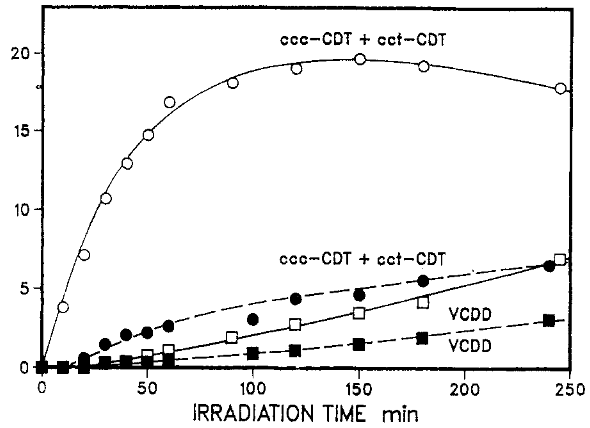


Figure 4. Photolysis of methanol solutions through a Corex filter: the solid lines represent the system of CuCl·*ctt*-CDT (2.39 mM) with *ctt*-CDT (13.48 mM) and the dashed lines that of CuCl·*ttt*-CDT (2.39 mM) with *ttt*-CDT (13.48 mM).

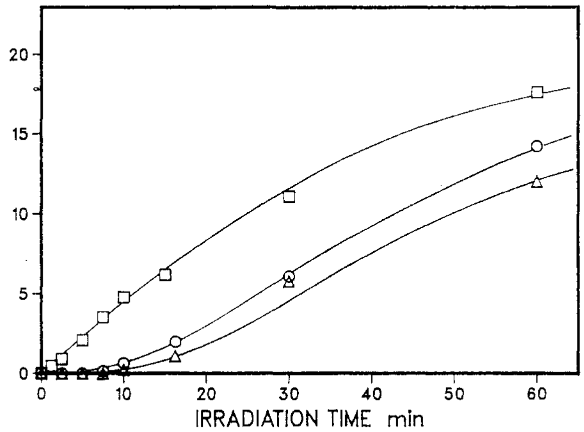
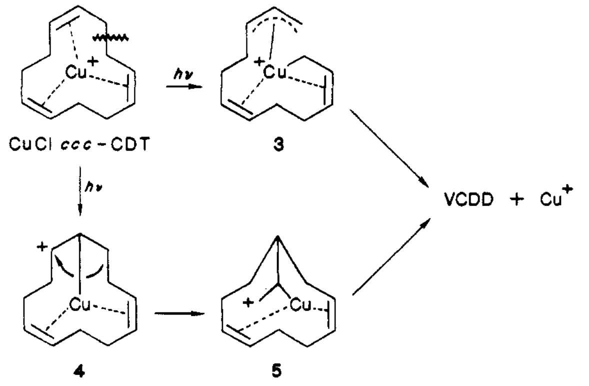


Figure 5. The photolysis of CuCl·CDT complexes alone: △ for CuCl·*ttt*-CDT, ○ for CuCl·*ctt*-CDT, and □ for CuCl·*ccc*-CDT.

For a skeletal rearrangement as complex as the present one, there must be a number of reasonable mechanisms available to reach VCDD from *ccc*-CDT. In view of the propensity of cyclic 1,5-polyenes to give vinyl-substituted carbacycles by photoexcitation, such as 1,[10] 2,[11] and 4-vinylcyclohexene (from 1,5-COD),[7] it is surmised that there might be a common pattern of pathways for these photorearrangements. Among the possible mechanisms the following two are most economical and straightforward in accommodating the observations.



The first is a photoinitiated allylic scission to give a η^1,η^3

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(13) Takakis, I. M.; Agosta, W. C. *J. Org. Chem.* **1979**, *44*, 1294.
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copper(III) complex, **3**, which undergoes reductive elimination to give VCDD. This is an insertion-type reaction to a bond doubly allylic to two olefinic bonds, and the copper center is formally in the +3 oxidation state. The second is a photoinduced transformation of a η^2 copper(I)–alkene complex to a η^1 copper(I)–carbenium ion **4**, so-called photocupration proposed by Salomon and coworkers.[15] The overall bond reorganization in **4** → **5** is similar to previous ones. In both cases, cis,cis configurations of remaining two double bonds are preserved. The tendency of the 1,5-cyclopolyenes, but not others, to undergo the vinyl group formation leads us to favor the former mechanism.

The wavelength dependency of photoreactions in the present case and in the CuCl·*ct*-1,5-COD case[8] may be a general phenomenon in photochemistry of metal complexes. While it indicates excitations to two different electronically excited states, as yet there is no compelling reason to assume that the two types of reactions, the cis–trans isomerization and rearrangements, occur on the separate energy surfaces of the different excited states (e.g., adiabatic reactions); nor are such experimental proofs readily obtainable. Alternatively, the observations of the deep-seated rearrangements, e.g., CuCl·*ct*-COD → TCO and CuCl·*ccc*-CDT → VCDD, by a higher energy (240–290 nm) but not by a lower energy (>290 nm) excitation, may be straightforwardly interpreted as a relation of pure energy supply and requirements during radiationless decays from the two excited states. Radiationless transition from an upper excited state should provide sufficient vibrational energy to overcome the activation barriers needed for highly energy demanding reactions, e.g., a α-bond scission or strained ring formation, but, on the other hand, that from a lower excited state affords only enough energy to cause a cis–trans isomerization.

Experimental Section

The equipment and materials were the same as those described in ref 8. FT-IR spectra were recorded with Bruker IFS 85 spectrophotometer. Commercial products of *ctt*-CDT (Aldrich) and *ttt*-CDT (Chemical Sample Co.) were distilled under vacuum; *ccc*-CDT was prepared from *ttt*-CDT by a known method.[12] The CuCl complex of CDT's were prepared by the method described before.[3] The UV data of these complexes were as follows CuCl·*ttt*-CDT, λ_{max} 234 nm (ϵ 510) and 290 (sh, 230); CuCl·*ctt*-CDT, λ_{max} 220 (sh, ϵ 385) and 225 (sh, 120); CuCl·*ccc*-CDT, λ_{max} 233 (300) and 260 (sh, 150). The photolysis apparatus and procedure including the analysis method were the same as those in the previous report.[8]

Photolysis of CuCl·CDT Complexes in the Presence of CDT. Reaction Pattern. A solution of CuCl·CDT, alone or with an excess of a CDT ligand, in methanol was irradiated under nitrogen with an appropriate filter. At intervals, 1 mL of the photolysate was withdrawn and treated with ammonium hydroxide solution and solid NaCN. The aqueous solution was extracted with ether and analyzed by GC. With use of a Pyrex filter, the deposition of copper(0) precipitates was not serious after 72 h. But, for experiments with a Corex filter, the deposition of copper(0) precipitates slowly coated the exposed surface: in less than a 10-h irradiation the exposed surface remained clear.

GC analysis was carried out with a OV-1 capillary column (12.5 m × 0.2 mm), isothermal at 120 °C to give the following peaks; 3.82 min for *ttt*-CDT, 4.02 min for VCDD, 4.32 min for *ctt*-CDT, 4.69 min for *cct*-CDT + *ccc*-CDT, and 9.30 min (trace) for an unknown compound. At the lower temperature of 100 °C the fourth peak was resolved to two at 12.26 and 12.49 min. The former was shown to be *ccc*-CDT by a coinjection with an authentic sample.

A mixture of *ccc*-CDT (21.8%) and *cct*-CDT (78.2%) was isolated by preparative GC and flash chromatography. This sample showed IR absorptions at 3013, 976(s), 736, and 700 cm^{-1} and MS (CI) peaks at *m/e* (%) 163 (M + 1$^+$, 100), 149 (82), 135 (60), 121 (62), 109 (66), and 95 (53).

Photolysis at Low Temperatures. At 77 K. Liquid nitrogen (100 mL) was placed in a Dewar bottle equipped with a quartz window. A slow stream of dry nitrogen was used to purge for 10 min. CuCl·*ctt*-CDT (0.82 mM) in methanol was injected with a syringe while nitrogen was stirred vigorously to disperse the solution as small solids. This was irradiated with OSRAM-HBO 200-W high-pressure lamp through a Vycor filter. Samples were scooped up and worked up to give an organic portion for GC analysis. The relative percent of *ttt*-CDT, *ctt*-CDT, *cct*-CDT + *ccc*-CDT, and VCDD were as follows; at 20 min, 14.0, 47.4, 31.4, and 0%; at 30 min, 15.9, 41.5, 34.5, and 0.15%; at 40 min, 14.5, 42.3, 34.1, and 0.16%.

Preparation of VCDD. A solution containing *ctt*-CDT (2 g, 12.3 mmol) anb CuCl·*ctt*-CDT (100 mg, 0.39 mmol) in methanol (160 mL) under nitrogen was irradiated through a Corex filter. A black copper metal deposited on the cell wall slowly and was removed every 24 h by washing with dilute nitric acid; each time CuCl·*ctt*-CDT (50 mg) was added to maintain the concentration. After a 250-h irradiation, GC analysis showed the yields of VCDD and CDT to be 52% and 26%, respectively. Methanol was evaporated. The residue was treated with ammonium hydroxide (5%, 200 mL) followed by solid sodium cyanide to discharge the blue color. Extraction with ether (3 × 100 mL) and evaporation afforded the crude products. The crude product was flash chromatographed on silica gel impregnated with 10% $AgNO_3$ twice to give VCDD in 99% purity. The sample was kept under N_2 atmosphere and stored in the freezer. Preparative GC on Carbowax 3M gave pure VCDD: MS (by CI, isobutane), *m/e* (%) 163 (M + 1, 100), 149 (89), 135 (42), 121 (61), 109 (36); MS (by EI), *m/e* (%) 162, 147, 133, 119, 105; FT-IR (relative intensity) 3076.29 (40), 3004.93 (100), 1656.76 (31), 1637.48 (61), 1471.61 (78), 993.29 (60), 910.35 (93), 736.80 (75), 709.77 (70) cm^{-1}; ^{13}C NMR 143.78, 131.14, 129.36, 128.30, 127.58, 112.33, 42.04, 31.76, 29.38, 26.36, 26.25, 22.63 ppm; ^{1}H NMR 5.83 (1 H, J = 10.2, 17.4, 6.8 Hz), 5.50 (2 H, J = 11.0 Hz), 5.33 (2 H, J = 11.0 Hz), 4.98 (ddd, 1 H, J = 17.4, 2.0, 1.8 Hz), 4.93 (ddd, 1 H, J = 10.2, 2.2, 1.0 Hz), 2.58 (m, 2 H), 2.44 (m, 1 H), 2.32 (m, 1 H), 2.28 (m, 1 H), 2.25 (m, 2 H), 2.00 (m, 2 H) 1.57 (m, 1 H), 1.49 (m, 1 H) ppm. VCDD stored under nitrogen in a freezer showed no changes after 4 months. Exposed in the air at room temperature, it became an insoluble solid.

VCDD was hydrogenated in ethanol in the presence of a Pt catalyst to give an oil that was distilled: MS, *m/e* (%), 168 (21), 167 (84), 125 (16), 164 (67), 97 (100); ^{1}H NMR ($CDCl_3$) 0.80 (t, 3 H, J = 7 Hz), 1.23 (2 H, dq, J = 7.0, 7.5 Hz).

VCDD–AgO_3SCF_3 Complexes. Dry THF solution (4 mL) containing AgO_3SCF_3 (49 mg, 0.19 mmol) was kept under nitrogen purging: VCDD (31 mg, 0.19 mmol) was added dropwise. Evaporation of solvent afforded powders which was recrystallized from THF–methylene chloride–hexane (2:2:1) to afford white microcrystals (31 mg): mp 145 °C dec; MS (by FAB mode) *m/e* 367, 365, 363 ($Ag_2SO_3CF_3^+$), 327, 325, 323, 321 (Ag_3^+), 271, 269 ($AgC_{12}H_{18}^+$). Anal. Calcd for $C_{12}H_{18}$ $(AgO_3SCF_3)_3$: C, 19.31; H, 1.94. Found: C, 18.99; H, 1.92.

To the mother liquor was added few drops of hexane, and the mixture was kept in a freezer compartment overnight to afford needles (28 mg): mp 107–109 °C sublimation; MS (by FAB mode), the same as above. Anal. Calcd for $C_{12}H_{18}\cdot AgO_3SCF_3$: C, 37.25; H, 4.33. Found: C, 36.86; H, 4.14.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, Ottawa, for generous financial support.

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