The structures of **2**,[4a] **4**,[4b] **5**,[4c] and **6**[4d] were determined via single-crystal X-ray diffraction; important bond distances and angles are given in the table. The complex **2** has a structure that is almost identical with its alkyl analogue, **1**.[1] The main feature of interest is the P-P distance of 2.053 (1) Å, which is slightly longer than the values 2.039 (1) Å reported for **1** and 2.034 Å recently reported for the free ligand.[5] These slight increases are expected in view of the more electronegative amido substituent reducing the electron density in the bonding orbitals of the P-P link and σ-donation reducing the repulsion between the phosphorus lone pairs. The P-N distance in **2** (1.682 (2) Å) is significantly shorter than in the free ligand (1.769 Å). This is probably due to a substantial reduction in the repulsive interaction between the nonbonding electron pairs on nitrogen and phosphorus. The probable structure of **3** involves a $(Me_3Si)_2NP{=}PN(SiMe_3)_2$ unit in which one of the phosphorus atoms behaves as a two-electron donor to $Cr(CO)_5$. This has been assigned on the basis of ^{31}P NMR and elemental analysis and by analogy to the known structure of its isoelectronic alkyl analogue.[6]

Both **4** and **6** may be thought of a derivatives of the ligand :P̈(or As)$N(SiMe_3)_2$ in which the main group 5 center is in a formally 1+ oxidation state and behaves as a two-electron donor to each chromium (0) atom. The phosphorus and arsenic centers in each molecule are planar and may be regarded as being approximately sp^2 hybridized. The remaining empty p orbital may behave as a π-acceptor via overlap with chromium d orbitals. The Cr-P distances, 2.290 (1) and 2.286 (1) Å, are similar to those found in complexes with π-acceptor phosphines such as $[Cr(CO)_5P(OPh)_3]$ (Cr-P = 2.309 (1) Å) and *trans*-$[Cr(CO)_4(P(OPh)_3)_2]$ (Cr-P = 2.252 (1) Å).[7]

For the arsinidene ligand, available data concern arsine ligands which are unlikely to be good π-acceptors and give Cr-As distances varying between 2.405 (2) and 2.516 (2) Å.[8] It can be argued that the M-As distances for arsenic π-acceptor ligands should, like their phosphorus counterparts, be similarly reduced so that a value somewhat less than 2.4 Å would be predicted. This predicted value is very close to that found in **6**, 2.381 (1) Å. It therefore seems that both phosphinidene and arsinidene ligands behave as four-electron donor and two-electron π-acceptor ligands. In **4** and **6** the P-N and As-N distances are normal, and the shortening expected from π-donation by the nitrogen p orbital is significantly reduced by a corresponding Si-N d-pπ interaction.

Compound **5** is the only known transition-metal complex in which the metal is bonded to two phosphinidene ligands. The bond distances and angles surrounding phosphorus are very similar to those in **4**. The terminal Cr-P distances of 2.323 (2) and 2.318 (2) Å are slightly longer than the central Cr-P distances of 2.279 (2) and 2.287 (2) Å. This is probably due to the fact that on the central chromium two phosphinidenes are trans to each other while at the terminal chromium they are trans to carbonyl. The planes defined by Cr_tPNCr_b and Cr_bPNCr_t are at ~96° with respect to each other so that the core geometry resembles that of allene.

NMR data are as follows: $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, relative to external 85% H_3PO_4) **2** δ 403.9, **3** (d of d) δ 534.5, 542.3, 556.5, and 564.3, J_{PP} = 631 Hz. ^1H NMR (C_6H_6) **2** δ 0.54, **3** δ 0.52, **4** δ 0.46, **6** δ 0.33, **7** δ 0.35. More complete spectroscopic studies involving IR, UV-vis, and other NMR data will be reported in a full account of this work.

In summary the presence of both phosphene and phosphinidene complexes in the same reaction mixture suggests a close interrelationship. Work is in progress to determine the mechanism of formation of these interesting species.

Acknowledgment. We are grateful to the NSF (CHE-8116355) for generous financial support.

Registry No. 2, 87829-45-6; **3**, 87829-46-7; **4**, 87829-47-8; **5**, 87829-48-9; **6**, 87829-49-0; **7**, 87829-50-3; **8**, 54036-90-7; **9**, 76505-23-2; $Na_2Cr(CO)_5$, 51233-19-3.

Supplementary Material Available: Summary of data and structure refinement, listing of atom coordinates, temperature factors, and bond distances and angles, and structure factor tables (75 pages). Ordering information is given on any current masthead page.

(4) Crystal data with Mo Kα radiation (λ = 0.71069 Å) T = 140 K: (a) **2**, triclinic $P\bar{1}$ (No. 2), a = 8.598 (2) Å, b = 9.983 (2) Å, c = 10.964 (3) Å, α = 71.38 (2), β = 85.23 (2), γ = 68.37 (2)°; Z = 1; μ = 11.5 cm^{-1}; 2166 unique data, 191 parameters; R = 0.025. (b) **4**, monoclinic, $P2_1/n$ (No. 14); a = 8.586 (4) Å, b = 18.284 (10) Å, c = 15.859 (7) Å, β = 90.74 (4); Z = 4; μ = 10.56 cm^{-1}; 4387 unique data, 307 parameters, R = 0.046. (c) **5**, orthorhombic *Pcab*, a = 16.751 (5) Å, b = 19.542 (3) Å, c = 25.546 (6) Å; Z = 8; μ = 9.9 cm^{-1}; 6055 unique data, 287 parameters, R = 0.055. (d) **6**, monoclinic $C2/c$, a = 16.784 (5) Å, b = 10.479 (4) Å, c = 17.434 (4) Å, β = 126.45 (2)°; Z = 4; μ = 23.3 cm^{-1}; 2049 unique data; 156 parameters; R = 0.029.

(5) Niecke, E.; Rüger, R.; Lysek, M.; Pohl, S.; Schoeller, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 486-487.

(6) Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.*, in press.

(7) Plastas, H. J.; Stewart, J. M.; Grim, S. O. *Inorg. Chem.* **1973**, *12*, 265-272. McAuliffe, C. A.; Levason, W. "Phosphine, Arsine and Stibine Complexes of the Transition Elements"; Elsevier: Amsterdam, 1979; Chapter 3, pp 74-90.

(8) Vahrenkamp, H. *Chem. Ber.* **1972**, *105*, 1486-1495. Cotton, F. A.; Webb, R. *Inorg. Chim. Acta.* **1974**, *10*, 127-132. Einstein, R. D.; Jones, R. D. G. *Inorg. Chem.* **1973**, *12*, 1148-1151. Huttner, G.; Schmid, H.-G.; Frank, A.; Orama, O. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 234.

Retention of Chirality during Thermal Automerization of Methyl 1,2-Diphenylcyclopentane-1-carboxylate

W. von E. Doering* and Ludmila Birladeanu

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received September 8, 1983
Revised Manuscript Received October 31, 1983

Many observations on single rotational epimerizations in optically active cyclopropanes reveal a preference of one group to rotate over another.[1] The strongest recorded preference involves methyl 1,2-diphenylcyclopropane-1-carboxylate, where the rotational propensity, R_A = 18, strongly favors rotation of the phenyl hydrogen carbon.[2] In terms of the well-known hypothesis of diradical qua intermediate protected by a barrier to reclosure of ~9 kcal/mol,[3] this observation is hard to explain.

A single example, 1-cyano-2-vinylcyclobutane (R_A = 1.48) reveals the phenomenon in a cyclobutane ring but at a reduced level.[4] No diastereomeric cyclopentanes have been examined, although thermal rearrangements of cyclopentane and two monosubstituted derivatives are reported.[5]

As depicted in Figure 1 for methyl 1,2-diphenylcyclopentane-1-carboxylate (**1**), the situation in cyclopentanes is qualitatively different owing to the accessibility of five conformations of an intermediary diradical, each protected against reclosure by at least one rotational barrier of the *n*-butane type.

Compound **1** commends itself for study for its close relation to the corresponding cyclopropane[2] and the radical-stabilizing effectiveness of its substitutents (estimated E_a ~ 48 kcal/mol vs. ~80 kcal/mol for cyclopentane).[6]

We report here its thermal epimerization with a surprisingly high degree of retained optical activity. Work is in progress to refine R_A by extrapolation to zero time and to establish the configurational relation required to identify which group has the higher rotational propensity.

Its synthesis, outlined in Figure 2, was thwarted by the failure of the most drastic conventional methods to effect hydrolysis of

(1) (a) Doering, W. von E.; Barsa, E. A. *Tetrahedron Lett.* **1978**, 2495-2498; (b) *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *78*, 2355-2357.

(2) Doering, W. von E.; Robertson, L. A.; Ewing, E. E. *J. Org. Chem.*, in press.

(3) Dervan, P. B.; Dougherty, D. A. In "Diradicals"; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; pp 107-149.

(4) Doering, W. von E.; Mastrocola, A. R. *Tetrahedron, Suppl. 1* **1981**, *37*, 329-344.

(5) King, K. D.; Goddard, R. D. *Int. J. Chem. Kinet.* **1981**, *13*, 755-770 and references cited therein.

(6) Doering, W. von E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279-5283.

0002-7863/83/1505-7461$01.50/0

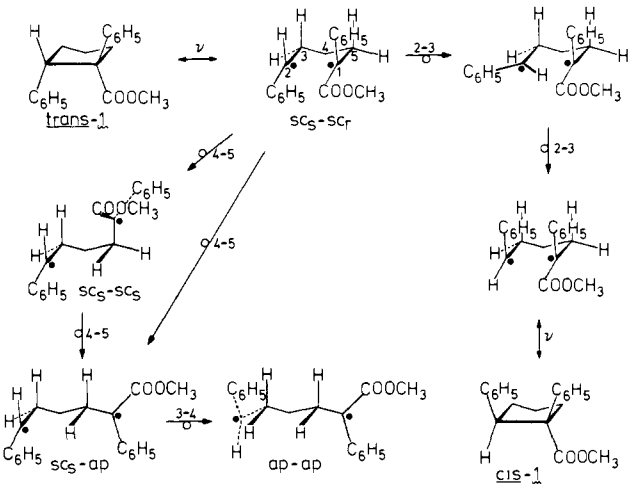

Figure 1. The path from *trans*-**1** to *cis*-**1** passes through the vibrational diradical, sc_s–sc_r, and over the continuous diradical as transition state by a C_2–C_3 internal rotation. The conformations on the lower left represent three of the five intermediary diradicals protected by the ~3-kcal/mol barriers around C_3–C_4 and C_4–C_5. [sc = synclinal; ap = antiperiplanar; subscripts s and r = left- and right-handed helix; 3–4 on arrow = rotation about bond between C_3 and C_4; ν over arrow = stretching vibrational mode.]

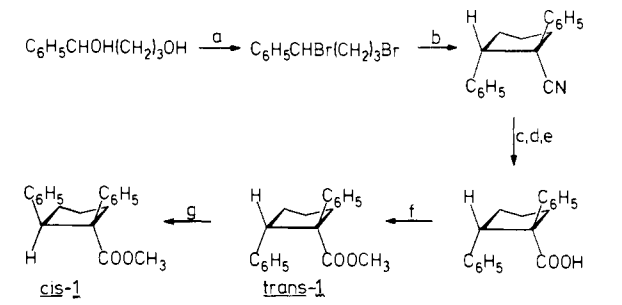

Figure 2. The synthesis of optically active *trans*-**1** is shown: (a) PBr_3; (b) phenylacetonitrile/C_6H_5–$CH_2N(C_2H_5)_3Cl$/NaOH; (c) diisobutylaluminum hydride; (d) tetra-*n*-butylammonium permanganate; (e) quinine; (f) diazomethane; (g) 400 °C, 15 min.

the nitrile until a two-step, reductive-oxidative procedure was developed. Even here, the highly hindered intermediate aldehyde resisted oxidation by conventional procedures, but could be oxidized by permanganate under conditions of phase transfer.[7]

The structure of *trans*-**1** rests on the method of synthesis, the exact mass (*m/e* 280.1465), the NMR [δ 7.45–7.20 (m, 10), 3.89 (dd, 1, J = 7.91, 13.84 Hz), 3.25 (s, 3), 2.21 (m, 1), 2.15 (m, 4), 2.12 (m, 1)], and the IR (1700 cm^{-1}) spectra.

cis-**1** is obtained in 39% yield on heating *trans*-**1** at 400° C for 33 min in decalin containing diphenylamine (50% of *trans*-**1** recovered) (the same result is obtained in the absence of diphenylamine and in diphenyl ether as solvent with or without diphenylamine): *m/e* 280.1465; NMR δ 7.14–6.85 (m, 10), 4.11 (t, 1, J = 7.2 Hz), 3.67 (s, 3), 2.62–2.56 (m, 2), 2.55–1.84 (m, 4); IR 1700 cm^{-1}.

The rearrangement is not effected, nor is deuterium incorporated in recovered *trans*-**1**, when *trans*-**1** is heated in perdeuterotoluene at 200 °C with 1 mol equiv of di-*tert*-butylperoxide.

In the presence of $Eu(fod)_3$, the benzylic hydrogen atom in *trans*-**1** shows a lanthanide-induced shift (LIS) of 0.80 relative to CH_3O as 1.00, while *cis*-**1** shows a relative shift of 1.44. The chiral LIS reagent, $Eu(hfbc)_3$, in perdeuterocyclohexane splits the CH_3O in *rac-trans*-**1** and *rac-cis*-**1** but gives good base-line separation only with the latter.

Resolution of the trans acid is effected partially by the quinine salt and is completed by recrystallization (CH_3OH) of the free acid to constant rotation: $[\alpha]^{25}_{589}$ −182° (*c* 0.733, $CDCl_3$). The enantiomer is obtained from the mother liquors: $[\alpha]^{25}_{589}$ +180° (*c* 0.508, $CDCl_3$).

Thermal rearrangement of optically active *trans*-**1** (0.207 g; $[\alpha]^{25}_{589}$ −132°; 73% of optical purity) in decalin (3.4%) containing 0.24 mol equiv of diphenylamine is effected by heating for 15 min at 400 °C. Analysis by capillary GLC of volatile recovered material (87%) shows 20.2% *cis*-**1** (>99.9%; $[\alpha]^{25}_{589}$ +20.1°; 40% of optical purity by chiral LIS), 65.2% recovered *trans*-**1** (containing 0.9% (+)-*cis*-**1**; $[\alpha]^{25}_{589}$ −93.3°; 52% of optical purity (corrected); 14.5% enantiomerization); and 14.6% unidentified products.

Corrected for 73% optical purity of starting *trans*-**1**, *cis*-**1** consists of 77.4% (+) and 22.6% (−), corresponding to an R_A factor of 3.4. When corrected for partial racemization of *trans*-**1** by assuming an average optical purity of *trans*-**1** of 62.5%, R_A becomes 4.5.

The dramatic degree to which chirality is retained in the face of unprecedented flexibility of the cyclopentadiyl system is understandable, if not uniquely so, in terms of the continuous diradical hypothesis outlined in Figure 1. To the extent that leakage over the 3 kcal/mol barriers aggravates enantiomerization in *cis*-**1** and recovered *trans*-**1** by generating intermediary diradicals, trapping by the likes of thiophenol becomes an exciting possibility.

Acknowledgment. We gratefully acknowledge that this material is based upon work supported by the National Science Foundation under Grant CHE-80-19427.

Registry No. (−)-**1**, 87883-15-6; (+)-**1**, 87883-16-7.

(7) Sale, T.; Sargent, M. W. *J. Chem. Soc., Chem. Commun.* **1978**, 253–254.

Surface-Enhanced Raman Scattering Study of Bipyridyl-Modified Ag Electrodes

Therese M. Cotton,* Dwarakannath Kaddi, and Dan Iorga

Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Received June 10, 1983

We have observed enhancement of the electron-transfer rate between cytochrome *c* and a Ag electrode in the presence of 4,4′-bipyridine and have studied the origin of this effect using cyclic voltammetry and surface-enhanced Raman scattering (SERS) (a discussion of this technique may be found in references cited in ref 1). The results indicate that a Ag(I)–bipyridine complex forms on the electrode surface, and this complex has the appropriate redox properties to mediate cytochrome oxidation and reduction. This study illustrates an important application of SERS for the determination of chemical and mechanistic information about electrodes modified through adsorption.

Redox proteins generally exhibit poor electron-transfer kinetics at metal or semiconductor electrodes for reasons that are not well understood.[2] Cytochrome *c* has been one of the most frequently studied proteins by electrochemical techniques. Except in a few instances,[3] it behaves irreversibly in the absence of mediators. Recently, chemical modifications of electrode surfaces have been used to overcome the sluggish response of proteins at electrodes.[4]

(1) (a) Van Duyne, R.P. In "Chemical and Biochemical Applications of Lasers"; Moore, C. B., Ed.; Academic Press: New York, 1979; Vol. 4, Chapter 5. (b) Chang, R. K., Furtak, T. E., Eds. "Surface Enhanced Raman Scattering"; Plenum Press: New York, 1982.

(2) Haladjian, J.; Bianco, P.; Serre, P. A. *Bioelectrochem. Bioenerg.* **1979**, *6*, 555 and references cited therein.

(3) (a) Yeh, P.; Kuwana, T. *Chem. Lett.* **1977**, 1145. (b) Bowden, E. F.; Hawkridge, R. M.; Chlebowski, J. F.; Bancroft, E. E.; Thorpe, C.; Blount, H. N. *J. Am. Chem. Soc.* **1982**, *104*, 7641.

0002-7863/83/1505-7462$01.50/0