1-adamantanecarboxylic acid, work equally well.

Derivatives are readily accommodated. Thus, diphenylacetic acid yields the corresponding aldehyde in a yield of 91%. Similarly, 6-bromohexanoic acid is readily converted to the aldehyde in a yield of 98%. Dicarboxylic acids, such as 1,10-decanedicarboxylic acid, provide the corresponding aldehydes in a yield of 97%. Finally, it is possible to reduce the half-ester of adipic acid to the corresponding ester aldehyde almost quantitatively.

Just as in the reduction of carboxylic acids with borane–tetrahydrofuran, the reduction of aromatic acids with thexylchloroborane is much more sluggish. The reaction requires 24 h and the yields are significantly lower and vary with the substituent. For example, both benzoic and *p*-anisic acids give yields of 51–59%, whereas, *p*-cyano- and *p*-nitrobenzoic acids give substantially better yields (83–86%).

Fortunately, the reduction of acid chlorides by LTBA is especially favorable for aromatic derivatives. Consequently, the two procedures complement each other, with the thexylchloroborane being ideal for aliphatic derivatives and the LTBA method being ideal for aromatic derivatives.

The remarkable difference in rates in the reduction by thexylchloroborane of aliphatic carboxylic acids, on the one hand, and aromatic carboxylic acids, on the other, suggests the possibility of achieving the selective reduction of a carboxylic acid group attached to an aliphatic or alicyclic moiety in the presence of a carboxylic acid group attached to an aromatic moiety. This possibility was tested in the following manner. A mixture of equimolar amounts of cyclohexanecarboxylic acid and benzoic acid was treated with 3 mmol equiv of thexylchloroborane (2 for hydrogen evolution and 1 for reduction). After 1-h reaction at room temperature, GC analysis of the product revealed a 93% yield of cyclohexanecarboxaldehyde, with only traces of benzaldehyde.

We explored several methods for the isolation of aldehyde products. We encountered no significant problems with such isolation. However, the well-known bisulfite procedure[11] appeared to be broadly applicable. Consequently, this procedure was adopted for our exploration of the scope of the reaction.

The following procedure for the reduction of 6-bromohexanoic acid is representative. An oven-dried, 100-mL flask, fitted with a side arm and a bent adapter connected to a mercury bubbler, was flushed with nitrogen and charged with 10.53 g (54 mmol) of 6-bromohexanoic acid and 16 mL of methylene chloride. The flask was immersed in an ice-water bath and a precooled solution of thexylchloroborane–dimethyl sulfide (39.6 mL, 3 M, 118.8 mmol, 10% excess) in methylene chloride was added dropwise with vigorous stirring. After the complete evolution of the hydrogen, the ice-water bath was removed and the reaction mixture was stirred for 15 min at room temperature. Analysis of an aliquot with 2,4-dinitrophenylhydrazine indicated a yield of 98%: mp of the hydrazone, 92–93 °C. Anal. Calcd: C, 40.12; H, 4.21; N, 15.60; Br, 22.25. Found: C, 39.97; H, 4.23; N, 15.59; Br, 22.07.

The rest of the reaction mixture (50 mmol) was transferred via a double-ended needle to the flask containing 50 mL of cold water in an ice-water bath and then hydrolyzed with vigorous stirring for 1 h at room temperature. The mixture was saturated with sodium chloride and the organic layer was separated.

After neutralization with a small amount of sodium bicarbonate, the organic layer was poured into 75 mL of a saturated aqueous sodium bisulfite solution and 70 mL of tetrahydrofuran was added. The mixture was stirred for 1 h. At this time the crystalline bisulfite adduct of 6-bromohexanal was apparent. The solution was cooled in an ice-water bath to ensure complete crystallization of the adduct. The adduct was then collected by filtration and washed with 3 × 25 mL of pentane and dried. The adduct was placed in 50 mL of a saturated aqueous magnesium sulfate solution and then 50 mL of pentane and 8 mL of a 37% formaldehyde solution were added. The mixture was stirred for 1 h. The pentane layer was separated and dried with anhydrous magnesium sulfate. Evaporation of all volatile materials gave an 86% yield of the almost pure product.

Distillation of the crude product gave 6.8 g (76%) of pure 6-bromohexanal: bp 106–107 °C (14 mm); n^{20}_D 1.4788. Anal. Calcd: C, 40.24; H, 6.19; Br, 44.63. Found: C, 40.12; H, 5.89; Br, 44.35.

Acknowledgment. The research support provided by the United States Army Research Office (Grant DAAG 29-79-C-0027) is gratefully acknowledged.

---

[11] Cornforth, J. W. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 757.

A Novel Olefin Bridged Dinuclear Arylpalladium Compound. X-ray Crystal Structure of $[\overline{\mathrm{NMe_2CH_2C_6H_4P}}\mathrm{d}\text{-}\mu\text{-}\{\mathrm{C(CF_3)}{=}\mathrm{C(CF_3)C(CF_3)}{=}\mathrm{C(CF_3)}\}\overline{\mathrm{PdCH(SiMe_3)C_6H_4N}}\mathrm{Me_2}]$

Fida Maassarani and Michel Pfeffer*

Laboratoire de Chimie de Coordination, ERA 670 CNRS
Institut Le Bel, Université Louis Pasteur
F-67070 Strasbourg Cêdex, France

Guy Le Borgne

Laboratoire de Cristallochimie, LA 254 CNRS
F-35042 Rennes Cêdex, France

Erik Wehman and Gerard van Koten

Anorganisch Chemisch Laboratorium
J.H. van't Hoff Instituut, University of Amsterdam
Nieuwe Achtergracht 166
1018 WV Amsterdam, The Netherlands

Received June 11, 1984

Directed C–C bond formation between different organo groups at a neutral metal center has become an important route in organic synthesis for the construction of new molecules.[1] It is now well established that cyclopalladated molecules, especially those with nitrogen as the donor atom, are reactive intermediates in this purpose.[2] Recently we showed that alkynes may readily insert into the Pd–C bonds of cyclopalladated tertiary amines.[3] In the course of our studies to shed some light on the selectivity of these new C–C bond formations we investigated the reactivity of $[\mathrm{Pd\{CH(R)C_6H_4NMe_2\text{-}2\}R'}]$ (**a**, R′ = 2-(dimethylamino)methylphenyl (dmba); **b**, R′ = 8-methylquinoline (8-mq); Scheme I) with R = H (**1**) or $\mathrm{SiMe_3}$ (**2**) toward $\mathrm{CF_3C{\equiv}CCF_3}$. Whereas **1** did not lead to any identifiable organometallic product,[3] we now report that the novel trimethylsilyl derivative **2** reacts readily to give selective asymmetric oxidative coupling of the cyclometallated organo groups and formation of a novel unsymmetrical dinuclear Pd species containing a bridging dimer of the alkyne.

Reaction of α-lithiated 2-(dimethylamino)-α-(trimethylsilyl)methylbenzene with the chloro-bridged dimers $(\mathrm{PdClR'})_2$ afforded in good yields the bicyclic compounds **2** (Scheme I). A crystal structure of analogous $\mathrm{Pd[CH(SiMe_3)C_6H_4NMe_2\text{-}2][C_6H_4CH(Me)NMe_2\text{-}2\text{-}(S)]}$ (**2c**), which exists as one diastereomeric pair, unambigously proved the cis geometry of this class of compounds.[4]

Compounds **2a** and **2b** reacted with excess of $\mathrm{F_3CC{\equiv}CCF_3}$ to give compounds **3a** (ca. 20%) and **3b** (ca. 60%), respectively, together with 1 equiv of the oxidative coupling product (e.g., **4b**; FD mass spectra, *m/e* 348 found (calcd *m/e* 348)). The elemental

---

[1] See, for instance: Trost, B. M. *Tetrahedron* **1977**, *33*, 2615.

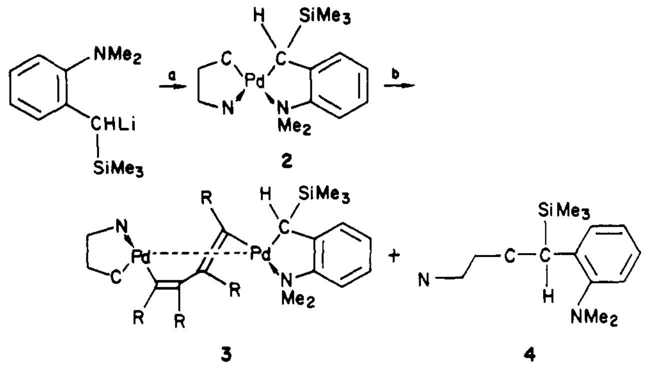
[2] Thompson, J. M.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 2667. Chao, C. H.; Hart, D. W.; Bau, R.; Heck, R. F. *J. Organomet. Chem.* **1979**, *179*, 301. Holton, R. A. *Tetrahedron Lett.* **1977**, 355.

[3] Bahsoun, A.; Dehand, J.; Pfeffer, M.; Zinsius, M.; Bouaoud, S. E.; Le Borgne, G. *J. Chem. Soc., Dalton Trans.* **1979**, 547. Arlen, C.; Pfeffer, M.; Bars, O.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1535.

[4] Maassarani, F.; Pfeffer, M.; Le Borgne, G.; van Koten, G.; Wehman, E., manuscript in preparation.

0002-7863/84/1506-8002$01.50/0

Scheme I. Synthesis



^{a} [(C$\frown$N)PdCl]$_2$, Et$_2$O, room temperature; C$\frown$N = 2-(dimethylamino)methylphenyl (dmba, a), 8-methylquinoline (8-mq, b). ^{b} $CF_3C{\equiv}CCF_3$ (excess), toluene, room temperature.

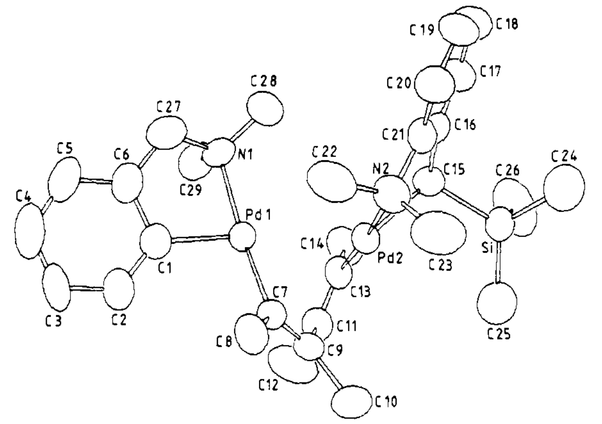
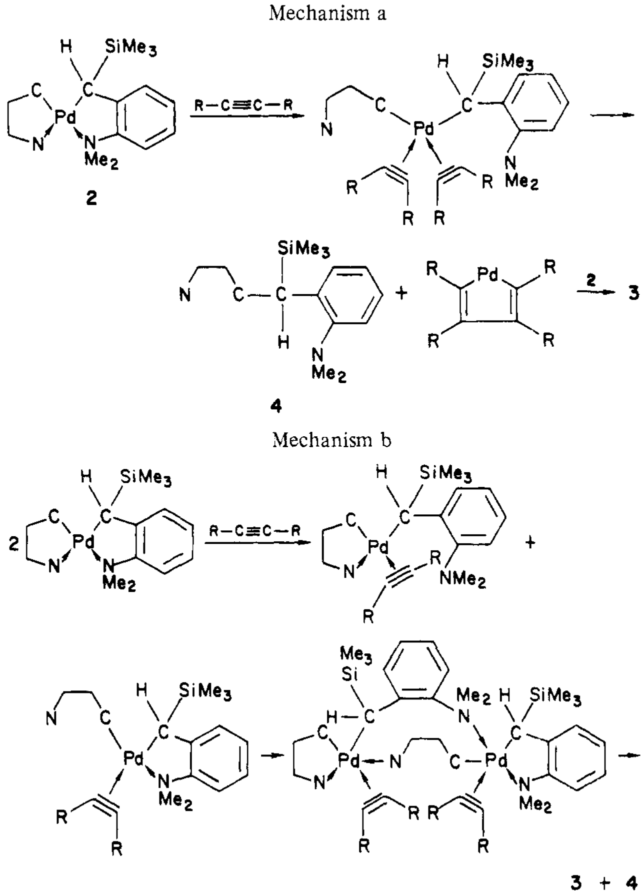


Figure 1. Molecular structure of **3a** (the fluorine and hydrogen atoms are omitted for clarity. Some relevant bond lengths: Pd(1)–N(1) 2.121 (6), Pd(1)–C(1) 1.979 (8), Pd(1)–C(7) 2.031 (8), C(7)–C(9) 1.33 (1), C(9)–C(11) 1.55 (1), C(11)–C(13) 1.30 (1), Pd(2)–C(13) 2.023 (7), Pd(2)–N(2) 2.177 (6), Pd(2)–C(15) 2.042 (8), Pd(1)–Pd(2) 2.756 (1) Å. Some relevant bond angles: N(1)–Pd(1)–C(1) 85.2 (3)°, C(1)–Pd(1)–C(7) 99.3 (3)°, N(1)–Pd(1)–C(7) 173.4 (3)°, N(1)–Pd(1)–Pd(2) 108.8 (2)°, C(1)–Pd(1)–Pd(2) 158.5 (2)°, C(7)–Pd(1)–Pd(2) 67.0 (2)°, N(2)–Pd(2)–C(15) 82.5 (3)°, C(15)–Pd(2)–C(13) 98.3 (3)°, N(2)–Pd(2)–C(13) 176.3 (3)°, N(2)–Pd(2)–Pd(1) 107.8 (2)°, C(15)–Pd(2)–Pd(1) 130.9 (2)°, C(13)–Pd(2)–Pd(1) 68.8 (2)°.

analysis and FD mass spectra[5] (**3a**, found *m/e* 876 (calcd *m/e* 876); **3b**, found *m/e* 884 (calcd *m/e* 884)) pointed to a dinuclear structure. In order to determine unambigously the geometry of these new compounds a single X-ray diffraction study was undertaken on **3a**. Crystal data: $C_{29}H_{32}F_{12}N_2Pd_2Si$, M_r 877.46, orthorombic, space group $P2_12_12_1$, $a = 10.793$ (11) Å, $b = 16.037$ (4) Å, $c = 19.445$ (9) Å, $U = 3365.7$ Å^3, $Z = 4$, $D_c = 1.73$ g cm^3, μ(Mo Kα) = 11.7 cm^{-1}, current $R = 0.0499$ ($R_w = 0.0648$) for 3432 reflections, observed [$I > 3\sigma(I)$] intensities (Enraf-Nonius CAD-4 diffractometer) with $1° < \theta < 28°$.

As shown in Figure 1 the molecule contains a tetrakis(trifluoromethyl)-substituted 1,4-dipallado-1,3-butadiene moiety. The C4 chain is σ-bonded to both Pd(1) and Pd(2) via C(7) and C(13), respectively. The new C–C bond between the linked alkynes is typical for a single bond (C9–C11 = 1.55 (1) Å) which is flanked at both sides by an isolated double bond (1.33 (1) and 1.30 (1) Å) with no indication of delocalization along the C4 chain. Such a feature has already been described in the case of [$Pt_3(CF_3C_2CF_3)_2(C_4(CF_3)_4)COD_2$] where a similar type of bridging hexafluorobut-2-yne dimer was found between two Pt atoms.[6]

Scheme II



The two metallocycles have the expected geometry (cf. the structural features of the five-membered chelate rings in **2c**[4]). The interesting point of this novel structure is the apparent planar coordination geometry about each of the Pd atoms which, however, *a priori seems to comprise only three ligands, i.e., the* N and the two C donor atoms. The nature of the fourth interaction, which would complete the square planar configuration, is not obvious, and three possibilities can be put forward: (i) A η^2 C=C→Pd bonding for which the C=C units seem to be well positioned is possible cf. ref 7, but with unusually long Pd—C bonds. (ii) The coordination around Pd(2) can be completed by a donative interaction of the C(7)—C(9) double bond of the butadiene ligand,[8] this would leave Pd(1) three-coordinate. However, a donative interaction of Pd(2) to Pd(1) would complete the four-coordination about Pd(1). Pd(2) seems to be well situated for such an interaction of its filled dz^2 orbital to Pd(1) (cf. bond angles in Figure 1).[9] (iii) There may be no interaction at all. The latter possibility would imply that the Pd centers are coordinatively unsaturated as a result of the *constraints* in the bridging butadiene ligand and the presence of the bulky SiMe$_3$ substituent. Whether the latter group plays a role in both the formation of [$\overline{NMe_2CH_2C_6H_4Pd}$-

---

(5) Calculated value for the Pd dimer. Found value is the highest peak in the molecular ion mass spectrum.

(6) Smart, R. E.; Browning, J.; Green, M.; Laguna, A.; Spencer J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1777.

(7) Note that Pd(2)···C(7) = 2.702 (10) Å and Pd(2)···C(9) = 2.706 (9) Å are shorter than Pd (1)···C(13) = 2.766 (10) Å and Pd(1)···C(11) = 2.954 (10) Å.

(8) The π interaction with only C(7)–C(9) and not with C(11)–C(13) is consistent with the fact that Pd(2) is closer to the former unit than Pd(1) from the latter one.[7] Moreover the midpoint of C7–C9 is only at 0.42 Å from the best plane defined by Pd(2), N(2), C(13), and C(15), whereas the midpoint of C(11)–C(13) is at 1.63 Å from the corresponding plane Pd(1), N(1), C(1), C(7).

(9) The rather short Pd–Pd distance of 2.756 (1) Å, which falls near to the range of Pd–Pd distance found for other dinuclear Pd complexes (2.57–2.70 Å),[10] compares well with that found in a dinuclear Pt(II) complex where such a donative interaction was found.[11]

(10) Bender, R.; Braunstein, P.; Dusausoy, Y.; Jud, J. M. *Inorg. Chem.* **1983**, *22*, 3394.

(11) Frew, A. A.; Manojlovic-Muire, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1980**, 624.

μ-{$C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)$}$\overline{\mathrm{PdCH(SiMe_3)C_6H_4N}}$-$Me_2$] and the stabilization of the dinuclear structure is under investigation.

A mechanism for the formation of these dinuclear Pd compounds must account for both the exclusive formation of the unsymmetric coupling product **4** and the fact that the Pd centers bear different ring systems, whereas these are present in a 1/1 ratio in the mononuclear Pd starting product. A possible route involves intramolecular oxidative coupling of the cyclometalated rings induced by coordination of the butynes with subsequent formation of a palladocyclopentadiene. Reaction of this intermediate with unreacted **2** may then form a dinuclear species which finally forms **3** via an intramolecular exchange of the organo groups (bridging C groups; Scheme IIa).[12]

However, a likely alternative, in view of our earlier findings concerning the insertion of butynes in Pd–C bonds, comprises prior formation of a dinuclear Pd intermediate containing both a $\overset{\frown}{NC}$ bridging dmba or 8-mq and a $Me_2NC_6H_4CH(SiMe_3)$ group as well as the coordinated butyne. Subsequent intramolecular C′–C coupling reactions of both the bridging $\overset{\frown}{CN}$ ligand and the two butynes then forms **3** (Scheme IIb).

Our present studies are directed to find further support for the mechanistic as well as the bonding aspects of these novel compounds.

Acknowledgment. We thank the CNRS for partial support and Dr. A. L. Spek for helpful discussion.

Registry No. 2a, 93184-75-9; **2b**, 93184-76-0; **3a**, 93184-77-1; **3b**, 93184-78-2; **4a**, 93184-79-3; **4b**, 93184-80-6; $(PdCl(dmba))_2$, 18987-59-2; $(PdCl(8\text{-mg}))_2$, 28377-73-3; $F_3CC{\equiv}CCF_3$, 692-50-2; α-lithiated 2-(dimethylamino)-α-(trimethylsilyl)methylbenzene, 93184-81-7.

Supplementary Material Available: NMR data for **2a**,**b**, **3a**,**b**, and **4b** and a molecular structure diagram (2 pages). Ordering information is given on any current masthead page.

---

(12) Van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *222*, 155.

(13) Examples of alkyne oligomerization on dimetallic centers have already been described in the literature,[14] but to our knowledge this is the first such case where this occurs between nonequivalent metal atoms.

(14) Dickson, R. S.; Fraser, P. J.; Gatehouse, B. M. *J. Chem. Soc., Dalton Trans.* **1972**, 2278. Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1269.

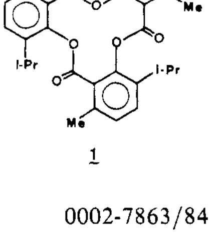
Heterogeneous Chirality Transfer on Photooxygenation

Raymond Gerdil, Giacomo Barchietto, and
Charles W. Jefford*

Department of Organic Chemistry
University of Geneva, 1211 Geneva 4, Switzerland

Received August 8, 1983

Asymmetry is usually induced in an organic reaction by employing chiral reagents and catalysts.[1] Under special circumstances, the chirality associated with polarized light[2] and crystal lattices[3] has also been used. We now report a novel case of induction where the dissymetric cavities within tri-*o*-thymotide (**1**) crystals[4] impart asymmetry to the reaction of an enclathrated substance.



1

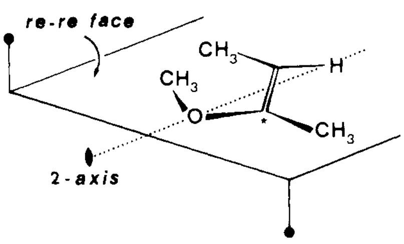
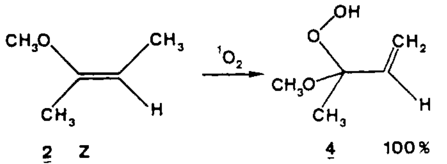
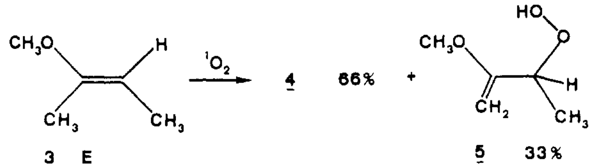


Figure 1. Idealized view of an orientation of the guest molecule **2** relative to the crystallographic 2-fold axis within the cavity of the TOT clathrate (**1**). Only the planar conformer is shown. The dissymmetric environment is schematized by the two symmetrically equivalent points associated with the mean olefinic molecular plane.

As suitable, prochiral guest molecules, (*Z*) and (*E*)-2-methoxybut-2-enes (**2** and **3**) where chosen. These enol ethers readily undergo dye-sensitized photooxygenation to give allylically rearranged hydroperoxides. The *E* isomer **3** gives two different racemic hydroperoxides **4** and **5**, whereas the *Z* isomer gives just hydroperoxide **4** as a pair of enantiomers (**4**-*S* and **4**-*R*). Moreover, both enol ethers **2** and **3** form crystalline clathrates with tri-*o*-thymotide (**1**). However, the *E* isomer **3** gave achiral, triclinic crystals. Fortunately, the more tractable *Z* isomer **2** furnished *chiral*, trigonal crystals having space group $P3_121$, a = 15.562 (1) Å, c = 30.383 (3) Å; Z = 6.





Crystals of opposite handedness were separated from the clathrate **1**/**2** by sorting single crystals manually and by assigning their chirality from polarimetric measurements made on small chips. Two samples of 100% optically pure clathrate (**1**/**2**) were so obtained and assigned the *P*-(+) and *M*-(−) configurations[6,7] by X-ray analysis.[8,9] The clathrate is of the cage type, having

---

(1) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice-Hall: Englewood Cliffs, NJ, 1971. Izumi Y.; Tai, A. "Stereodifferentiating Reactions, The Nature of Asymmetric Reactions"; Academic Press: New York, 1977. Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1978**, *10*, 176–285. ApSimon, J. W.; Seguin, R. P. *Tetrahedron*, **1979**, *35*, 2797–2842. Valentine, D.; Scott, J. W. *Synthesis* **1978**, 329–356.

(2) Moradpour, A.; Nicoud, J. F.; Balavoine, G.; Kagan, H. B.; Tsoucaris, G. *J. Am. Chem. Soc.* **1971**, *93*, 2353–2354. Bernstein, W. J.; Calvin, M.; Buchardt, O. *J. Am. Chem. Soc.* **1972**, *94*, 494–498.

(3) Elgavi, A.; Green, B. S.; Schmidt, G. M. J. *J. Am. Chem. Soc.* **1973**, *95*, 2058–2059.

(4) (a) Gerdil, R.; Allemand, J. *Helv. Chim. Acta* **1980**, *63*, 1750–1753. (b) Gerdil, R.; Allemand, J.; Bernardinelli, G. *Acta Crystallogr., Sect. A* **1981**, *A37*, C92. Arad-Yellin, R.; Green, B. S.; Knossow, M.; Tsoucaris, G. *J. Am. Chem. Soc.* **1983**, *105*, 4561–4571.

(5) Hammond, W. B. *Tetrahedron Lett.* **1979**, *25*, 2309–2312.

(6) In solution, tri-*o*-thymotide (**1**) adopts chiral, propeller-like, left-handed (*M*) and right-handed (*P*) conformations which rapidly interconvert.[7] However, cocrystallization of **1** with a suitable guest, which is the case for **2**, occurs with spontaneous resolution so that any single crystal consists entirely of **1** fixed in the *M* or *P* configuration.

(7) Downing, A. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc. B* **1970**, 24.

0002-7863/84/1506-8004$01.50/0