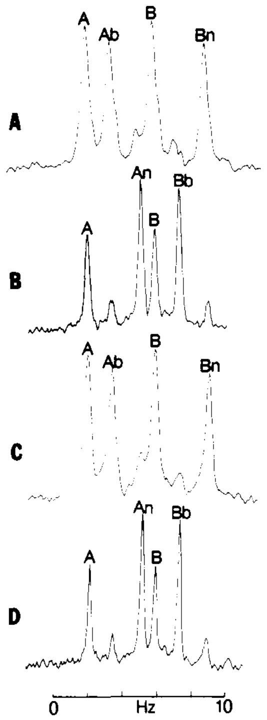
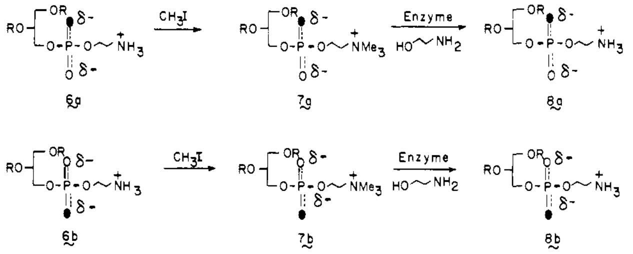


Figure 1. ^{31}P NMR spectra (at 81.0 MHz) of the silylated products of DPPE from **6a** (A, 36 μmol, 500 scans, line broadening 0.2 Hz), **6b** (B, 24 μmol, 1100 scans, line broadening 0.1 Hz), **8a** (C, 10 μmol, 2000 scans, line broadening 0.2 Hz), and **8b** (D, 20 μmol, 3500 scans, line broadening 0.1 Hz). Spectral parameters: Spectral width 500 Hz, 16K data points, ^{1}H decoupling, 60° pulse, repetition time 16 s.

The observed ^{31}P NMR spectra (at 81.0 MHz) of the silylated products[14] of **6a** and **6b** are shown in Figure 1,A and B, respectively, which shows a 1.45 Hz (0.018 ppm) and a 3.1 Hz (0.038 ppm) shift for bridge and nonbridge ^{18}O, respectively. The spectral analysis is summarized in Table I, which shows that **6a** contains 55% ^{18}O, 72% isomer X, and 28% isomer Y, whereas **6b** contains 63% ^{18}O, 17% isomer X, and 83% isomer Y. The optical purity remains to be improved by a detailed investigation.[15] Samples of higher isotopic purity (>95%) have been obtained, but the partially enriched samples were preferred for the present study.

Despite the imperfect optical purity and the indeterminate configuration of **6a** and **6b**, the stereochemical course of transphosphatidylation catalyzed by phospholipase D could be elucidated. Scheme III shows three most likely mechanisms for this conversion: (A) The reaction proceeds by a two-step process involving a phosphatidyl–enzyme intermediate; (B) the reaction proceeds by a single displacement; (C) the reaction is a reversal of hydrolysis. Although studies on the base exchange reaction have supported mechanism A,[10] there is no direct kinetic or stereochemical evidence to support A or to rule out B or C. A kinetic analysis is complicated by the fact that the reaction medium is heterogeneous.

Scheme IV. Stereochemistry of Transphosphatidylation Catalyzed by Phospholipase D



Our approach is outlined in Scheme IV. The [$^{18}O_1$]DPPE **6a** and **6b** were methylated with CH_3I to give [$^{18}O_1$]dipalmitoylphosphatidylcholine (DPPC) (**7a** and **7b**, respectively)[16] without affecting the configuration at phosphorus. The complete quaternization at nitrogen was characterized by ^{1}H NMR spectroscopy and TLC by comparing with authentic samples of DPPE and DPPC. Reaction of **7a** and **7b** separately with ethanolamine in H_2O/ether catalyzed by phospholipase D[18] gave DPPE **8a** and **8b**, respectively. The ^{31}P NMR spectra of the silylated products of **8a** and **8b** are shown in Figure 1,C and D, respectively. The spectral analysis in Table I indicates that the transphosphatidylation proceeds with complete retention of configuration and without detectable oxygen exchange.

On the basis of our results, mechanism C in Scheme III can be ruled out since it predicts an exchange of oxygen, assuming free rotation of the phosphoryl group. Mechanism B would predict an inversion of configuration based on the fact that all single-step phosphoryl-transfer reactions which have been studied proceed with inversion of configuration,[2-9] unless the mechanism in phospholipase is an exception which involves pseudorotation. On the basis of the overall retention in the stereochemistry, mechanism A seems to be the most probable mechanism for transphosphatidylation.

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(14) Although the ^{31}P NMR signal of DPPE is very broad due to aggregation, the silylated product gives very sharp signals since the O-silylated head group is no more amphiphilic. In Figure 1A–D, the silylation was performed with hexamethyldisilazane (e.g., 25 μmol of DPPE in 2.5 mL of $CDCl_3$, added with 50 μL of reagent) which gives exclusively O silylation as shown by ^{29}Si NMR Spectroscopy at 39.73 MHz (24.66 ppm relative to Me_4Si). The samples can easily be recovered after the NMR experiments.

(15) The loss of diastereomeric purity occurs most likely at the acid hydrolysis of **5a** and **5b**. However, incomplete isomeric purity of starting materials and incomplete separation of **5a** and **5b** may also contribute to a small extent.

(16) The methylation of DPPE under the condition described in ref 17 was found to give a wrong product. Complete and quantitative quaternization of DPPE was achieved by the methylation in a heterogeneous system: DPPE + CH_3I in $CHCl_3$/2 M aqueous K_2CO_3 + $Et_3N^+CH_2C_6H_5Cl^-$.

(17) Eibl, H. *Chem. Phys. Lipids* **1980**, *26*, 239.

(18) A typical reaction mixture contains, in 30 mL of H_2O, 30 μmol of DPPC, 1.2 mmol of $CaCl_2$, 1.2 g of ethanolamine, pH adjusted to 5.6 with HCl, 15 mL of ether, and proper amount of phospholipase D (cabbage, 1–2 IU/mg, Sigma). Stirring at room temperature overnight gives ca. 50% DPPE plus a small amount of phosphatidic acid. No reaction occurs in the absence of the enzyme.

Synthesis, Properties, and Molecular Structure of a Trivalent Organouranium Diphosphine Hydride[1]

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We have recently demonstrated that the hydrogenolysis of bis(pentamethylcyclopentadienyl)uranium(IV) chlorohydrocarbyls represents a clean and efficient route to new U(III) compounds.[2] An example is the synthesis of the chemically versatile, trimeric uranium(III) monochloride shown in reaction 1.[2] With the goal

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(1) Presented in part at: (a) The Fifteenth Rare Earth Research Conference, Rolla, MO, June 17, 1981. (b) Lanthanide and Actinide Chemistry Symposium, 28th IUPAC Congress, Vancouver, Canada, Aug 17, 1981.

(2) (a) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 5075–5078. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics*, in press.

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$$3U[(CH_3)_5C_5]_2(R)Cl + {}^3/_2H_2 \rightarrow \{U[(CH_3)_5C_5]_2Cl\}_3 + 3RH \qquad (1)$$

$$R = CH_3,\ CH_2Si(CH_3)_3,\ \text{etc.}$$

of extending this approach to the synthesis of other unusual, low-valent uranium complexes, we have now studied the hydrogenolysis of the corresponding bis(pentamethylcyclopentadienyl)uranium(IV) bis(hydrocarbyls)[3] in the presence of ligands compatible both with mononuclear structures[4] and low oxidation states. Phosphine complexes of f-element organometallic compounds are a virtually unexplored area,[5,6] and we report here the synthesis, molecular structure, and some of the properties of the novel uranium(III) bis(phosphine) hydride, $U[\eta^5\text{-}(CH_3)_5C_5]_2(dmpe)H$, dmpe = bis(1,2-dimethylphosphino)ethane.

Hydrogenolysis of $U[(CH_3)_5C_5]_2R_2$ complexes [$R = CH_3$, $CH_2Si(CH_3)_3$] proceeds smoothly at −20 °C in the presence of excess dmpe (1.2 equiv) according to reaction 2. Product **1**

$$U[(CH_3)_5C_5]_2R_2 + 1.5H_2\ (1\ \text{atm}) + \text{dmpe} \xrightarrow[18\ \text{h}]{\text{toluene}} \underset{\mathbf{1}}{U[(CH_3)_5C_5]_2(\text{dmpe})H} + 2RH \qquad (2)$$

$$R = CH_3,\ CH_2Si(CH_3)_3$$

separates from solution as black microcrystals and can be purified by vacuum Soxhlet extraction with toluene (isolated yield = 75%). All manipulations with this compound must be conducted under argon or helium, since it reacts with nitrogen (*vide infra*). Quantitative gasometric measurements verify the stoichiometry of reaction 2, i.e., 1.48 (5) equiv of H_2 are consumed. Anal. Calcd for $C_{26}H_{47}P_2H$: C, 47.34; H, 7.18; P, 9.39. Found: C, 47.14; H, 7.51; P, 9.31. Compound **1** is insufficiently soluble for cyroscopic molecular weight measurements.

Although the relatively slow U(III) electronic spin–lattice relaxation time results in substantial linewidths (lw),[3,7] 270-MHz ^{1}H NMR spectra of **1** are highly informative. Thus, at room temperature in C_6D_6 or $C_6D_5CD_3$, a singlet at δ −5.97 (lw = 18 Hz, 30 H) is observed which is typical in field position and breadth for an $\eta^5\text{-}(CH_3)_5C_5$ signal in a trivalent $U[(CH_3)_5C_5]_2(X)L$ compound.[2] The broad dmpe proton resonances at δ −11.8 (lw = 52 Hz, ca. 12 H) and −20.0 (lw = 91 Hz, ca. 4 H) suggest a symmetrical coordination environment on the room temperature NMR timescale, while variable temperature studies (vide infra) indicate that the instantaneous structure is of considerably lower symmetry. As is found for other $U[(CH_3)_5C_5]_2(X)L$ complexes,[2] exchange is observed in the NMR spectrum between coordinated and incrementally added free dmpe (L) (verified by magnetization transfer experiments). The uranium-bound hydride resonance could not be located in the proton spectrum, presumably a consequence of the large linewidth. The infrared spectrum of **1** (Nujol mull) exhibits, besides transitions attributable to $\eta^5\text{-}(CH_3)_5C_5$ [1022 (m), 801 (m) cm^{-1}][2,3] and coordinated dmpe [1281 (w), 1139 (w), 1080 (w), 947 (s), 932 (m), 918 (w), 830 (w), 729 (m), 718 (w), 633 (m) cm^{-1}][8] a very strong, broad band at 1219 cm^{-1} which shifts to 870 cm^{-1} ($\nu_H/\nu_D = 1.40$) in the analogue prepared with D_2. We assign this absorption to a U–H stretching mode. Interestingly, the energy of this transition is displaced to significantly lower energy than in tetravalent uranium hydrides.[3,9] The molar magnetic susceptibility of **1** at 295 K, 5120 × 10^{-6} emu ($\mu_{\text{eff}} = 3.47\ \mu_B$), was measured by the Evans method[10] and is consistent with a U(III) (5f^3) formulation.[11]

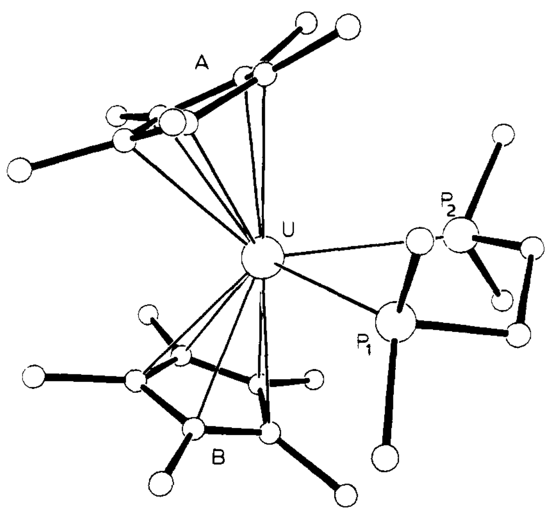

Figure 1. Perspective ORTEP drawing of the nonhydrogen atoms in the solid-state structure of $U[\eta^5\text{-}(CH_3)_5C_5]_2[(CH_3)_2PCH_2CH_2P(CH_3)_2]H$ (**1**). All atoms are represented by arbitrarily sized spheres for pusposes of clarity. The crystallographically independent pentamethylcyclopentadienyl ligands are denoted by labels A and B.

Black crystals of **1** suitable for diffraction studies were obtained by allowing a concentrated solution of $U[(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]_2$ and excess dmpe in toluene to stand under a hydrogen atmosphere. The crystals are orthorhombic, space group $Pca2_1\text{-}C_{2v}^5$ (No. 29)[12a] with a = 15.055 (5) Å, b = 11.052 (5) Å, c = 16.915 (6) Å, and Z = 4 (ρ_{calcd} = 1.56 g cm^{-3}; μ_a(Mo K$\bar{\alpha}$) = 5.58 mm^{-1}). Three-dimensional diffraction data (a total of 4000 independent reflections having $2\theta_{\text{MoK}\bar{\alpha}} < 58.7°$) were collected on a computer-controlled Nicolet P$\bar{1}$ autodiffractometer by using graphite-monochromated MoK$\bar{\alpha}$ radiation and full 1°-wide ω scans. The structural parameters have been refined to convergence [R(unweighted, based on F) = 0.058 for 2054 independent absorption-corrected reflections having $2\theta_{\text{MoK}\bar{\alpha}} < 58.7°$ and $I > 3\sigma(I)$] in cycles of empirically weighted full-matrix least-squares refinement which employed anisotropic thermal parameters[12b] for all nonhydrogen atoms.

The X-ray structural analysis reveals that single crystals of **1** are composed of discrete mononuclear $U[\eta^5\text{-}(CH_3)_5C_5]_2(dmpe)H$ molecules as shown in Figure 1. Each U(III) ion is π bonded to the planar (to within 0.03 Å) five-membered rings of both $(CH_3)_5C_5$ ligands in the familiar "bent sandwich" configuration[13] and is σ bonded to the (terminal) hydride and both phosphorus atoms of the chelating dmpe ligand. Thus, the U(III) ion in **1** is formally 9-coordinate with a coordination geometry which is likely (vide infra) quite similar to that of the Th(IV) ion in

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(3) (a) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939–3941. (b) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *Ibid.* **1981**, *103*, 6650–6667.

(4) Hydrogenolysis of $U[(CH_3)_5C_5]_2R_2$ compounds in aromatic solvents leads to the dimeric, tetravalent hydride $\{U[(CH_3)_5C_5]_2H_2\}_2$. This, in turn, can suffer hydrogen loss, yielding the trivalent hydride $\{U[(CH_3)_5C_5]_2H\}_x$.[3]

(5) Organolanthanide phosphine complexes. (a) $(Yb(C_5H_5)_3P(C_6H_5)_3)$: Fischer, E. O.; Fischer, H. *J. Organomet. Chem.* **1966**, *6*, 141–148. (b) $(Yb(C_5H_5)_3P(n\text{-}C_4H_9)_3)$: Marks, T. J.; Porter, R.; Kristoff, J. S.; Shriver, D. F. In "Nuclear Magnetic Resonance Shift Reagents"; Sievers, R. E., Ed.; Academic Press: New York, 1973, 247–264. (c) $(Yb\{N[Si(CH_3)_3]_2\}_2(dmpe))$: Andersen, R. A. "Lanthanide and Actinide Chemistry Symposium", 28th IUPAC Congress, Vancouver, Aug 17, 1981.

(6) Organoactinide phosphine complexes: (a) Reference 2; $(U[(CH_3)_5C_5]_2(Cl)P(CH_3)_3)$. (b) Reference 5c; $(MCl_4(dmpe)_2, M(CH_3)_4(dmpe)_2$, M = Th, U).

(7) Fischer, R. D. In "Organometallics of the f-Elements"; Marks, T. J., Fischer, R. D., Eds.; Reidel: Dordrecht, 1979; Chapter 11.

(8) (a) Butter, S. A.; Chatt, J. *J. Chem. Soc. A* **1970**, 1411–1415. (b) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687–2695.

(9) (a) Turner, H. W.; Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 2781–2782. (b) Typical $\nu_{M\text{-}H}$ values are 1359 cm^{-1} $(Th[(CH_3)_5C_5]_2[OC(CH_3)_3]H)$,[2b] 1480 cm^{-1} $(Th\{N[Si(CH_3)_3]_2\}_3H)$,[5a] and 1430 cm^{-1} $(U\{N[Si(CH_3)_3]_2\}_3H)$.[5a]

(10) (a) Ostfeld, D.; Cohen, J. A. *J. Chem Educ.* **1972**, *49*, 829. (b) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005.

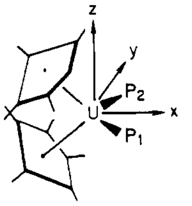
(11) (a) Kanellakopulos, B. In "Organometallics of the f-Elements"; Marks, T. J., Fischer, R. D., Eds.; Reidel: Dordrecht, 1979; Chapter 1 and references therein. (b) Because of the low solubility of **1**, the uncertainty in χ_M is estimated to be ±10%. Nevertheless, this value is at the high end of the range found for actinide (but not lanthanide) 5f^3 systems. Susceptibility studies in the solid state are in progress.

(12) (a) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 115. (b) See paragraph at end regarding supplementary material.

(13) (a) Petersen, J. L.; Lichtenbeger, C. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433–6441 and references therein. (b) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. F.; Denton, B.; Rees, R. V. *Acta Crystallogr., Sect. B.* **1974**, *B30*, 2290–2304 and references therein.

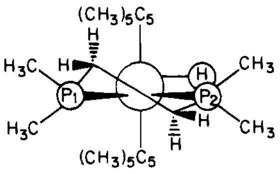
$\{Th[\eta^5\text{-}(CH_3)_5C_5]_2[\mu\text{-}CO(CH_2C(CH_3)_3)CO]Cl\}_2$, (**2**).[14]

Although it was not possible to locate the hydride ligand with the X-ray diffraction data, a reasonable position, which is in agreement with the low-temperature NMR data (vide infra), can be inferred from the positions of the other ligands in **1**. We define a Cartesian coordinate system which is centered on the U(III) ion (**A**) and has the *x* axis at the intersection of the "equatorial girdle" (the plane containing U which bisects the dihedral angle between the two C_5-ring mean planes) and the plane defined by U and the two C_5-ring centers-of-gravity (C_{ga} and C_{gb}). The *y* axis lies in the equatorial girdle parallel to both C_5-ring mean planes. Since steric factors in mononuclear bis(pentamethylcyclopentadienyl)methyl complexes are known to preclude any substantial displacements of coordinated noncyclopentadienyl atoms from the equatorial girdle,[2,14,15] the hydride ligand must lie in or very near the girdle. The orientation of the dmpe ligand in the equatorial girdle strongly argues that the hydride is in the vicinity of the positive *y* axis: P_1 is displaced from the C_{ga}–U–C_{gb} plane by 2.26 Å in the direction of the negative *y* axis while P_2 is displaced by 1.01 Å in the direction of the positive *y* axis. In contrast, the X ligands in $M[\eta^5\text{-}(CH_3)_5C_5]_2X_2$ actinide complexes[2,14,15] are usually symmetrically disposed about the *x* axis in the equatorial girdle. Therefore the most likely diffraction-derived position for the hydride ligand in **1** is in the equatorial girdle between the U–P_2 vector and the positive *y* axis—a position similar to that occupied by Cl in **2**.[14]



The C_{ga}–U–C_{gb} plane in **1** intersects the C_5-ring mean planes in angles of 89.1 and 90.0°, respecitvely, and the P_1–U–P_2 plane in a dihedral angle of 87.8°. Bond lengths and angles for selected chemically distinct groupings of atoms in **1** are U–C, 2.79 (3, 4, 7, 10) Å;[16] U–P_1, 3.211 (8) Å; U–P_2, 3.092 (8) Å; (cyclopentadienyl ring) C–C, 1.39 (4, 3, 6, 10) Å; (Cp ring to methyl) C–C, 1.55 (5, 3, 13, 10) Å; P–C, 1.78 (5, 11, 31, 6) Å; C_{ga}–U–C_{gb}, 136.2°; C_g–U–P_1, 105.4 (–, 3, 3, 2)°; C_g–U–P_2, 110.7 (–, 24, 24, 2°); P_1–U–P_2, 63.8 (2); U–P–C, 119 (2, 3, 9, 6)°;[16] C–P–C, 99 (2, 2, 4, 6)°.

As the temperature of **1** in $C_6D_5CD_3$ is lowered, the ^1H NMR methylene and methyl signals of coordinated dmpe broaden and collapse; the $\eta^5\text{-}(CH_3)_5C_5$ resonance also broadens. At –50 °C, the methylene resonances appear as two singlets, δ –35.8 (lw = 79 Hz, 2 H) and –26.4 (lw = 78 Hz, 2 H), and the methyl resonance as three singlets, δ –20.6 (lw = 47 Hz, 6 H), –15.8 (lw = 45 Hz, 3 H), –15.65 (lw = 45 Hz, 3 H); two pentamethylcyclopentadienyl resonances are observed at δ –8.65 (lw $\sim$ 25 Hz, 15 H) and –8.57 (lw $\sim$ 25 Hz, 15 H). That the splitting of the low field methyl and $\eta^5\text{-}(CH_3)_5C_5$ resonances is field and temperature dependent indicates that it is not scalar coupling[17] in origin. Rather, the slow exchange limit spectrum reflects the low symmetry (C_1) of the dmpe solution coordination environment (**B**), in accord with the solid-state crystallographic results.



B

In principle, the remaining magnetic nonequivalences as well as scalar coupling would be resolvable in the absence of the severe line broadening. Preliminary line-shape analysis indicates that exchange with free dmpe is slower than the site permutation process(es) within the coordinated dmpe. Presumably the latter involve reversible single phosphorus atom dissociation and/or "spinning" of the dmpe about the local C_2 axis together with inversion of the five-membered chelate ring. Evidence for the high chemical lability of the uranium-coordinated dmpe is provided by displacement reactions. Thus, NMR experiments indicate that **1** reacts rapidly with THF, CO, and N_2 to yield free dmpe and complex mixtures of U(III) and U(IV) products. The nature of these products is under investigation.

This study underscores the ready accessibility of organouranium phosphine complexes, as exemplified by a hydrogenolysis route to a trivalent diphosphine hydride, and suggests that such species will have a rich chemistry. Particularly noteworthy in the present case is the marked lability of the chelating bis(phosphine) and the formation of a *trivalent* product from reaction 2. Although the reaction mechanism has not been investigated in detail (reactions 1 and 2 likely proceed via unstable chloro- and alkylhydrides, respectively[2,3]), the absence of a divalent product analogous to the group 4B $Zr(C_5H_5)_2(dmpe)$[8b] is further evidence for a greater stability of formal oxidation states higher than +2 among the early actinides.[2,3]

Acknowledgment. We thank the National Science Foundation (CHE8009060) for generous support of this research.

Supplementary Material Available: Tables of fractional coordinates and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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[14] Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393–5396.

[15] (a) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1978**, *100*, 7112–7114. (b) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206–2220.

[16] The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

[17] Intra-dmpe couplings are expected to be on the order of only a few Hz. See ref 8b. Also see: Akhtar, M.; Ellis, P. D.; MacDiarmid, A. G.; Odom, J. D. *Inorg. Chem.* **1972**, *11*, ,2971–2921.

Total Synthesis of (±)-Triptonide and (±)-Triptolide

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Because the promising anticancer compound triptolide **1**[1] and congeners remain scarcely accessible from the natural source, interest in a practical total synthesis of these substances continues at a high level. Herein we report a new, efficient route to an established key intermediate in previous total syntheses of triptolide (**1**) and triptonide (**2**),[2] viz., 7-oxo-14-methoxyisodehydroabietenolide (**3**). The present sequence features two new methods of butenolide construction, one of which finds subsequent utilization in the assemblage of the benzenoid nucleus as an integral part of the synthesis rather than its origination in aromatic starting materials, as in prior approaches.[2] In addition, the pathway

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[1] (a) Kupchan, S. M.; Court, W. A.; Dailey, R. G., Jr.; Gilmore, C. J.; Bryan, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 7194. (b) Kupchan, S. M.; Schubert, R. M. *Science, (Washington, D.C.)* **1974**, *185*, 791. (c) *K'o Hseuh Tung Pao* **1977**, *22*, 458; *Chem. Abstr.* **1978**, *88*, 177077y.

[2] (a) Racemic triptonide and triptolide, Buckanin, R. S.; Chen, S. J.; Frieze, D. M.; Sher, F. T.; Berchtold, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 1200. (b) *l*-Triptolide and *l*-triptonide: van Tamelen, E. E.; Demers, J. P.; Taylor, E. G.; Koller, K. *Ibid.* **1980**, *102*, 5424.

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