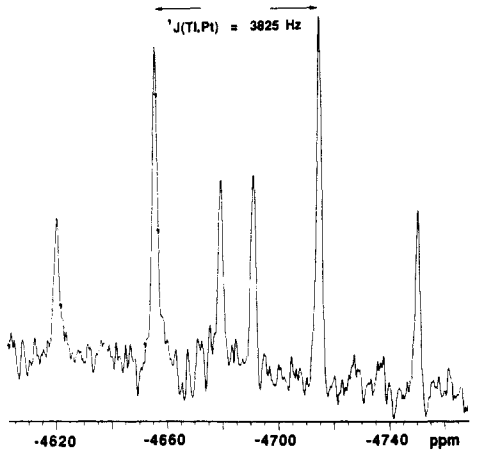

Figure 2. The 64.5-MHz $^{195}Pt\{^1H\}$ NMR spectrum of $[Tl(crown\text{-}P_2)Pt(CN)_2][NO_3]$ in chloroform at 20 °C.

Crown-P_2 was obtained in 86% yield by the condensation of diphenylphosphine, paraformaldehyde, and diaza-18-crown-6 in toluene at 60 °C.[5,6] Successive addition of thallium(I) nitrate and bis(triphenylphosphine)platinum(II) cyanide to **1** in a 1:1 v/v mixture of toluene and methanol gives a colorless solution from which white needles of $[Tl(crown\text{-}P_2)Pt(CN)_2]NO_3$ (**2**) (IR, ν(CN), 2133 cm^{-1}) were obtained after partial evaporation of the solvent followed by the addition of ethyl ether. The structure of the complex as determined by X-ray diffraction is shown in Figure 1.[7] The complex consists of a planar $P_2Pt(CN)_2$ unit that is capped by the diaza-crown portion with the thallium(I) ion sitting within it. Notice that the thallium is shifted out of the rough plane of the aza-crown moiety toward the platinum. The Tl-Pt distances in the two crystallography independent cations in the crystals of **2** (2.911 (2) and 2.958 (2) Å) are similar but considerably shorter than the Tl-Pt distance in $Tl_2Pt(CN)_4$ (3.140 (1) Å). Some of this shortening may be brought about by the presence of the ligand bridge, while another contribution arises from the difference in metal-metal bonding between the binuclear Tl-Pt unit in **2** and the trinuclear Tl-Pt-Tl unit in $Tl_2Pt(CN)_4$.

Complex **2** is soluble in a range of solvents (chloroform, dichloromethane, acetone), and it retains the Pt-Tl units when dissolved. The $^{31}P\{^1H\}$ NMR spectrum is a convenient probe of this since phosphorus coupling to both ^{195}Pt (33.8% natural abundance, $S = {}^1/_2$) and ^{205}Tl (70.5% natural abundance; ^{203}Tl (39.5%); both $S = {}^1/_2$) is observed (δ = 7.6 ppm, J(Pt,P) = 2293 Hz, J(Tl,P) = 41 Hz) in chloroform. However, the thallium ion can be removed. Treatment of a chloroform solution of **2** with a 20-fold excess of 18-crown-6 results in the disappearance of the ^{31}P NMR spectrum of **2** and the growth of new resonances of thallium-free $(crown\text{-}P_2)Pt(CN)_2$ (**3**) (δ = 2.0 ppm, J(Pt,P) = 2225 Hz) and no coupling to thallium.

The $^{195}Pt\{^1H\}$ NMR spectrum of **2** produces the first measure of a Tl-Pt one-bond coupling constant. The spectrum recorded in chloroform at 20 °C is shown in Figure 2. It consists of two triplets with δ = -4684 ppm, ^1J(Pt,P) = 2293 Hz, and ^1J(Pt,Tl) = 3825 Hz. This is the first observation of ^1J(Tl,Pt), and it gives, in conjunction with the short Pt-Tl distance, a clear indication that there is a significant covalent component to the Tl-Pt bond. Under the conditions of the experiment, it was not possible to resolve the difference between coupling to ^{205}Tl and ^{203}Tl.

The electronic spectral features of **2** are similar to those of $Tl_2Pt(CN)_4$ (luminescence, λ_{max} = 444 nm). In dichloromethane solution at 23 °C, irradiation of **2** in the ultraviolet range produces blue luminescence (λ_{max} = 451 nm). The luminescence is lost when the thallium is removed from **2** through the addition of 18-crown-6.

The hybrid ligand **2** has considerable potential for forming new complexes involving the coordination of transition metals and main group metal ions. Preliminary evidence for formation of Ir^I-Tl^I and Ir^I-Pb^{II} bonded units is already at hand,[8] and further extensions are under development.

Acknowledgment. We thank the National Science Foundation (CHE-8941209) for support, Johnson-Matthey, Inc., for a loan of platinum salts, and Dr. Marilyn M. Olmstead for crystallographic advice.

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and data collection parameters for **2** (12 pages). Ordering information is given on any current masthead page.

(4) For recent work on crown ethers bearing phosphine substituents and related macrocycles, see: Wei, L.; Bell, A.; Ahn, K.-H.; Hall, M. Mm.; Warner, S.; Williams, I. D.; Lippard, S. J. *Inorg. Chem.* **1990**, *29*, 825. Powell, J.; Gregg, M. R.; Kukis, A.; May, C. J.; Smith, S. J. *Organometallics* **1989**, *8*, 2918. Powell, J.; Kukis, A.; May, C. J.; Meindl, P. E.; Smith, S. J. *Organometallics* **1989**, *8*, 2933. Powell, J.; Gregg, M. R.; Meindl, P. E. *Organometallics* **1989**, *8*, 2942 and references in each.

(5) Colorless crystals: mp 110-112 °C dec. $^{31}P\{^1H\}$ NMR: δ = -26 ppm (s) ($CDCl_3$). ^1H NMR: δ = 2.96 (4 H, t), 3.43 (2 H, d), 3.53 (8 H, s), 3.55 ppm (4 H, t) in $CDCl_3$.

(6) Maier, L. *Helv. Chim. Acta* **1965**, *110*, 1034. McLain, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 6355. Balch, A. L.; Olmstead, M. M.; Rowley, S. P. *Inorg. Chim. Acta* **1990**, *168*, 255.

(7) Crystals for X-ray diffraction were obtained by diffusion of ethyl ether into a dichloromethane solution of **2**. Colorless **2**, $[Tl(crown\text{-}P_2)Pt(CN)_2][NO_3]\cdot 1.5H_2O\cdot 0.5CH_2Cl_2$, crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with a = 21.476 (7) Å, b = 14.274 (4) Å, c = 32.660 (9) Å, β = 104.36 (2)°, and Z = 8, at 130 K. R = 0.102 and R_w = 0.078 for 6586 reflections with $I > 2\sigma(I)$ and 435 parameters. The asymmetric unit contains two independent cations and two disordered nitrate ions, as well as lattice water and dichloromethane. The structures of the two cations are similar. When parameters are quoted, the first refers to cation A and the second to cation B. Data were collected with two different X-ray source tubes and merged; see supplementary material for details.

(8) Balch, A. L.; Neve, F., to be published.

Electronic Control of π-Facial Selectivities in Nucleophilic Additions to 7-Norbornanones

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School of Chemistry, University of Hyderabad Hyderabad 500 134, India

Received March 13, 1990

The role of stereoelectronic effects in controlling the face selectivity during nucleophilic additions to trigonal carbon atoms has come under intense and incisive mechanistic scrutiny in recent years.[1] In particular, substituted cyclohexanones have been explored extensively, although these systems have intrinsic limitations in the sense that the two π-faces of the carbonyl group are sterically nonequivalent and, therefore, not ideally suited for the segregation and assessment of steric vs electronic effects. In a pioneering study, employing sterically unbiased 5-substituted 2-adamantanones, le Noble[2] has drawn attention to the importance of the hyperconjugative assistance by electron-rich σ bonds to the adjacent antibonding orbitals (Cieplak effect)[3] to explain control of diastereoselectivity. It occurred to us that 2,3-endo,endo-disubstituted 7-norbornanones[4,5] can serve as excellent substrates

(1) For an authoritative background review and comprehensive list of references, see: Cieplak, A. S.; Tait, B. D.; Johnson, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 8447.

(2) (a) Cheung, C. K.; Tseng, L. T.; Lin, M.-H.; Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 1598. (b) Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 5873. (c) Lin, M.-H.; Cheung, C. K.; Chung, W. S.; Turro, N. J.; Srivastava, S.; Li, H.; le Noble, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 6562. (d) Chung, W. S.; Turro, N. J.; Srivastava, S.; Li, H.; le Noble, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 7882. (e) Lin, M.-H.; Silver, J. E.; le Noble, W. J. *J. Org. Chem.* **1988**, *53*, 5155.

(3) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540.

(4) While π-facial selectivities in nucleophilic additions to 7-keto norbornenes[5] and 7-keto benzonorbornenes[5] have been previously investigated, the stereochemical outcome in endo-substituted 7-norbornanones, to our knowledge, has surprisingly not received attention; see: Ashby, E. C.; Noding, S. A. *J. Org. Chem.* **1977**, *42*, 264.

(5) Okada, K.; Tomita, S.; Oda, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 459 and references cited therein.

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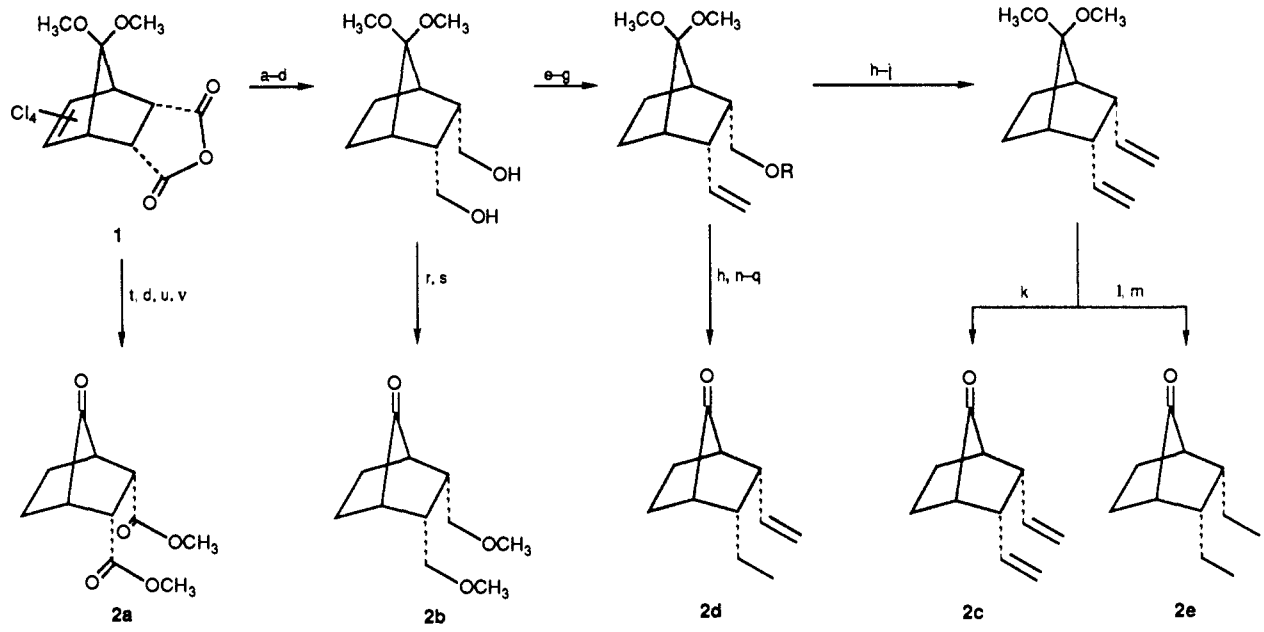
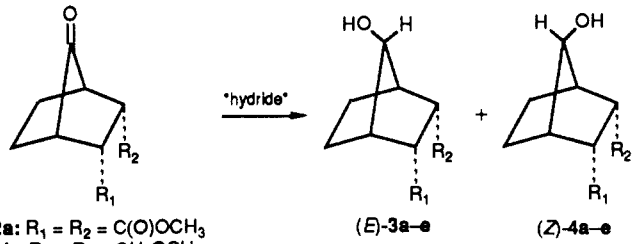
Scheme I[a]

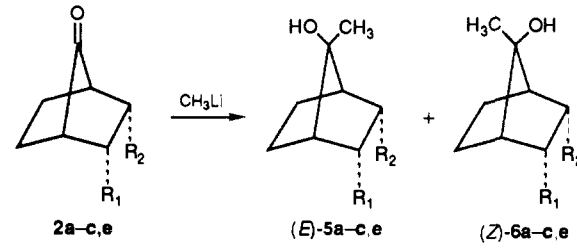


[a] Reagents and yields: (a) MeOH/H$^+$, reflux, 48 h, 53%; (b) LAH, ether, reflux, 5 h, 84%; (c) Na–Liquid NH_3, THF, 75%; (d) H_2, Pd–C, EtOAc, 20 psi, 95%; (e) TBDMSCl, NaH, THF, room temperature, 1.5 h, 79%; (f) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −60 °C, 30 min, 90% (crude); (g) $Ph_3P^+CH_3Br^-$, $C_5H_{11}O^-Na^+$, C_6H_6, room temperature, 88% (crude); (h) $(n\text{-}Bu)_4N^+F^-$, THF, room temperature, 93%; (i) f, 90% (crude); (j) g, 57%; (k) Amberlyst-15, moist $(CH_3)_2CO$, reflux, 55%; (l) H_2, PtO_2, EtOAc, 40 psi, 20 min, 95%; (m) k, 81%; (n) H_2, Pd–C, EtOAc, 40 psi, 45 min, 95%; (o) f, 86%; (crude); (p) g, 52%; (q) k, 60%; (r) NaH, MeI, THF, room temperature, 1.5 h, 70%; (s) k, 70%; (t) c, EtOH, NH_4Cl, 30%; (u) MeOH/H$^+$, reflux, 5–6 h, 70%; (v) 5% aqueous H_2SO_4, THF, reflux, 1.5 h, 72%.

Scheme II



Scheme III



for studying π-facial stereoselectivities, particularly for further testing the validity of the Cieplak model.[3] Besides having a sterically unbiased 7-keto functionality, the 2,3-endo,endo substituent in these substrates can provide a convenient handle for the electronic modification at the distal stereogenic center. Herein, we report the practical realization of this expectation and demonstrate that the electronic induction by the 2,3-endo,endo substituents dramatically alters the facial selection in nucleophilic additions to 7-norbornanones.

Five endo,endo-disubstituted 7-norbornanones **2a–e** were synthesized from the readily available Diels–Alder adduct **1**[6] of 5,5-dimethoxytetrachlorocyclopentadiene and maleic anhydride as shown in Scheme I.[7,8] The stereochemical assignments to **2a–e** follow from the unambiguous methods of synthesis and ^{13}C NMR data (see supplementary material), which indicated consistent shielding of the C_5,C_6 resonances (δ ~18–20 region) due to the C_2,C_3 endo,endo substitution.[9]

Reduction of **2a–e** with sodium borohydride, lithium aluminum hydride, and the bulky lithium tri-*tert*-butoxyaluminum hydride furnished a mixture of (*E*)-**3a–e** and (*Z*)-**4a–e** alcohols in each case in nearly quantitative yield, Scheme II. Addition of methyllithium to **2a–c,e** also furnished a mixture of (*E*)-**5a–c,e** and (*Z*)-**6a–c,e** tertiary alcohols in high yield (Scheme III). The results are summarized in Table I. Except in the case of **3b** and **4b**, all the diastereomeric pairs of 7-norbornanols were separated and fully characterized and their stereostructures unambiguously assigned on the basis of relatively greater deshielding of the C_2 and C_3 exo protons in *Z* alcohols as compared to the corresponding

Table I. Product Ratios in the Metal Hydride Reduction and Methyllithium Additions to **2a–e**

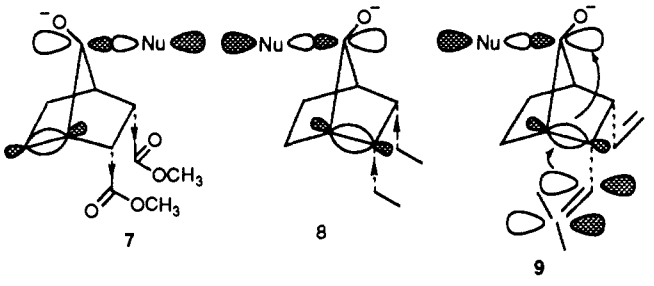
	E:*Z* distribn[a]			
substrate	$NaBH_4$[b,c]	$LiAlH_4$[b,d]	$(t\text{-}BuO)_3LiAlH$[b,d]	CH_3Li[d]
2a	84:16 (**3a**) (**4a**)	87:13 (**3a**) (**4a**)	77:23 (**3a**) (**4a**)	>90:<10 (**5a**) (**6a**)
2b	40:60[e] (**3b**) (**4b**)			34:66 (**5b**) (**6b**)
2c	36:64 (**3c**) (**4c**)	35:65 (**3c**) (**4c**)	34:66 (**3c**) (**4c**)	27:73 (**5c**) (**6c**)
2d	25:75 (**3d**) (**4d**)			
2e	20:80 (**3e**) (**4e**)	21:79 (**3e**) (**4e**)	29:71 (**3e**) (**4e**)	17:83 (**5e**) (**6e**)

[a] Ratios based on ^1H NMR integration of the total mixture (±5%). [b] Reductions were carried out at ~0–10 °C for 10 min–1 h till the starting ketone was fully consumed. Reactions were continuously monitored by TLC. [c] In Methanol. [d] In dry diethyl ether. [e] The *E*–*Z* mixture could not be separated for full characterization of each isomer.

(6) Newcomer, J. S.; McBee, E. T. *J. Am. Chem. Soc.* **1949**, *71*, 946.
(7) Relatively simple 2,3-endo,endo disubstituted 7-norbornanones are not quite readily accessible, and not many are reported in literature. The syntheses **2a–e** are routine but new and unambiguous.
(8) All new compounds reported here were fully characterized.
(9) Levy, G. C.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemistry*; Wiley-Interscience: New York, 1972.

E alcohols in the ^1H NMR spectrum.[8] This trend was further confirmed through Eu(fod)$_3$ induced shift reagent studies.

The results summarized in Table I demonstrate a very significant variation in face selectivity as a function of 2,3-endo,endo substitution, the most dramatic being the reversal in *E*:*Z* ratio in going from **2a** (84:16) to **2e** (20:80). The predominant approach of nucleophiles to the syn face in **2a** and to the anti face in **2e** is fully consonant with the prediction based on the Cieplak's hyperconjugative model[3] according to which delocalization of σ electrons in the electron-rich antiperiplanar bond into the incipient σ^* orbital lowers the transition-state energy as indicated in **7** and **8**, respectively. The anti-face preference in the case of **2b** and **2c**, having groups traditionally considered as electron withdrawing ($-I$),[10] is somewhat unexpected at first sight but may be attributed to through-space donation in a perpendicular conformation as shown in **9** for **2c**.[11]



7 8 9

In summary, we have shown for the first time that π-facial selectivities in nucleophilic additions to 7-norbornanones can be electronically fine-tuned, and further theoretical and experimental work is currently underway.

Supplementary Material Available: Tables of ^1H and ^{13}C NMR and LRMS/HRMS data on all key compounds mentioned in this paper along with copies of spectra (16 pages). Ordering information is given on any current masthead page.

(10) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Eastern: New Delhi, 1986; p 17.

(11) We thank Professor W. J. le Noble for this suggestion.

Synthesis of New Tricyclic Chiral P-H Bond Phosphoranes, "Triquinphosphoranes", from Chiral Diaminodiols. Asymmetric Addition on an Activated Carbonyl Compound

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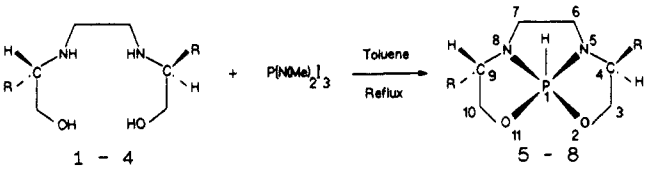
It is well-known that the P-H bond in hydridophosphoranes reacts with carbonyl compounds, leading to P–C bond formation.[1,2] However, to our knowledge, asymmetric addition of chiral hydridophosphoranes[3,4] to carbonyl compounds is without precedent. We report herein the synthesis (Scheme I) of a new class of tricyclic, chiral hydridophosphoranes, the "triquinphosphoranes",[5] from chiral diaminodiols, as well as their asymmetric addition to an activated carbonyl compound, ketopantolactone.[6]

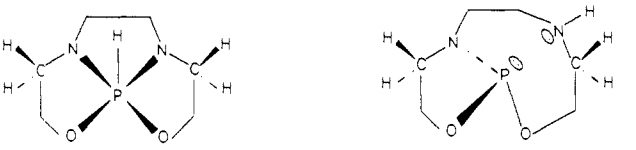
Scheme I[a]



1 - 4 5 - 8

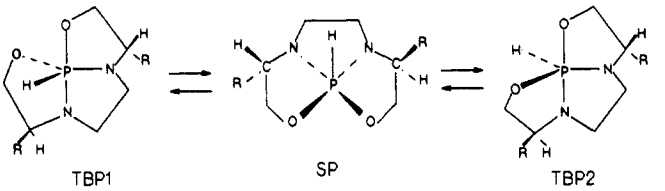
[a] **1** and **5**, R = H; **2** and **6**, R = CH_3; **3** and **7**, R = $CH(CH_3)_2$; **4** and **8**, R = CH_2Ph.

Scheme II



5 9

Scheme III



TBP1 SP TBP2

Compounds **5–8** were easily prepared in 80–90% chemical yields by the usual stoichiometric exchange reaction between diaminodiol[7] (0.3 M) (**1–4**) and hexamethylphosphorous triamide (1 equiv), in refluxing toluene under a nitrogen atmosphere, for 1 h.[8] Chiral C_2 symmetry axis diaminodiols **2–4** are particulary promising for the synthesis of chiral phosphoranes. They were synthesized in two steps from the methyl ester hydrochloride of the corresponding natural amino acid[9] (for **2**, (*S*)-(+)-alanine, **3**, (*S*)-(+)-valine; **4**, (*S*)-(−)-phenylalanine).

The $^{31}P\{^1H\}$ NMR spectra of these hydridophosphoranes exhibit only one single high-field signal ($\delta \approx -36.5$),[8] characteristic of 5-coordinated phosphorus compounds,[10] and a large coupling constant ($^1J_{PH} \approx 715$ Hz)[8] revealing a pronounced s character for the P-H bond. No signal was detected for the bicyclic alk-

(1) Laurenco, C.; Burgada, R. *Tetrahedron* **1976**, *32*, 2089. Germa, H.; Burgada, R. *Bull. Soc. Chim. Fr.* **1975**, *11-12*, 2607. Savignac, P.; Richard, B.; Leroux, Y.; Burgada, R. *J. Organomet. Chem.* **1975**, *93*, 331. Burgada, R.; Germa, H. *C. R. Seances Acad. Sci., Ser. C* **1968**, *267*, 270.

(2) Bouvier, F.; Vierling, P.; Dupart, J. M. *Inorg. Chem.* **1988**, *27*, 1099.

(3) (a) Klaebe, A.; Brazier, J. F.; Cachapuz Carrelhas, A.; Garrigues, B.; Marre, M. R.; Contreras, R. *Tetrahedron* **1982**, *38*, 2111. Klaebe, A.; Carrelhas, A.; Brazier, J. F.; Houalla, D.; Wolf, R. *Phosphorus Sulfur* **1977**, *3*, 61. Klaebe, A.; Brazier, J. F.; Mathis, F.; Wolf, R. *Tetrahedron Lett.* **1972**, 4367. (b) Newton, M. G.; Collier, J. F.; Wolf, R. *J. Am. Chem. Soc.* **1974**, *96*, 6888. Brazier, J. F.; Ferekh, J.; Munoz, A.; Wolf, R. *C. R. Seances Acad. Sci., Ser. C* **1971**, *272*, 1521. (c) Hellwinkel, D.; Willfinger, H. *Tetrahedron Lett.* **1969**, 3423. (d) Burgada, D.; Bon, M.; Mathis, F. *C. R. Seances Acad. Sci., Ser. C* **1967**, *265*, 1499. (e) Hellwinkel, D. *Chem. Ber.* **1966**, *99*, 3642.

(4) Jeanneaux, F.; Riess, J. G.; Wachter, J. *Inorg. Chem.* **1984**, *23*, 3036.

(5) (4*S*,9*S*)-4,9-Dialkyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo-[6.3.0.0^{1,5}]undecane: "triquinphosphorane" by analogy with the name "triquinacene" coined by Woodward et al. (*J. Am. Chem. Soc.* **1964**, *86*, 3162).

(6) Dihydro-4,4-dimethyl-2,3-furandione: ketopantolactone.

(7) *N*,*N*'-Bis(1-alkyl-2-hydroxyethyl)ethylenediamine: diaminodiol.

(8) After the removal of toluene under reduced pressure, the compounds were isolated by either distillation or recrystallization. **5** is obtained in 80% chemical yield: bp 75 °C/0.05 mmHg; $^{31}P\{^1H\}$ NMR δ −37.3 ($^1J_{PH}$ = 721 Hz). **6** (82%): bp 80 °C/0.05 mmHg; $[\alpha]^{22}_D$ +94.0° (*c* 1.18, $PhCH_3$); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ −37.1 ($^1J_{PH}$ = 711 Hz). **7** (85%): bp 110 °C/0.05 mmHg; $[\alpha]^{22}_D$ +28.6° (*c* 1.10, $PhCH_3$); $^{31}P\{^1H\}$ NMR δ −35.2 ($^1J_{PH}$ = 712 Hz). **8** (80%): mp 71 °C (recrystallized from cyclohexene); $[\alpha]^{22}_D$ +49.5° (*c* 0.98, $PhCH_3$); $^{31}P\{^1H\}$ NMR δ −36.3 ($^1J_{PH}$ = 723 Hz).

(9) (a) For compound **4**, see: Vriesema, B. K.; Lemaire, M.; Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1986**, *51*, 5169. (b) For an analogous compound with (*S*)-(−)-proline, see: Colombo, L.; Gennari, C.; Poli, G.; Scolastico, C. *Tetrahedron* **1982**, *38*, 2725. Marchelli, R.; Dradi, E.; Dossena, A.; Casnati, G. *Tetrahedron* **1982**, *38*, 2061. Lodi, T.; Marchelli, R.; Dossena, A.; Dradi, E.; Casnati, G. *Tetrahedron* **1982**, *38*, 2055.

(10) Tebby, J. C. *Methods in Stereochemical Analysis: Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, D. L., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; Vol. 8, p 40.

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