up the unit cell contents. These two hexamers are not identical but nearly so.

A less cluttered view of the hexagonal prism formed by the lithium atoms and the oxygen atoms is given in Figure 2. The six atoms forming either hexagonal face deviate by less than 0.1 Å from the best plane through the face.

Since all six enolate anions (i.e., $C_6H_{11}OLi$ units) in the crystallographic asymmetric unit of the pinacolone enolate are similar, a labeled plot of only one of these is given in Figure 3. Selected bond distances and angles for the specific enolate depicted are given with standard deviations of the least significant digits in parentheses. One salient feature is the variation in bond angles for the three C(2)–O(1)–Li bonds. Particularly outstanding are the rather large C(2)–O(1)–Li(1) bond angle (140.0 (4)°) and the small C(2)–O(1)–Li(2) bond angle (88.0 (9)°).

The average bond lengths of the six crystallographically independent enols corresponding to the bonds represented by C-(1)—C(2) and C(2)—O(1) in Figure 3 are 1.33 and 1.34 Å, respectively. These values match the values of the four C=C (1.34 Å) and the four C—O (1.35 Å) bonds in the symmetrical THF-solvated pinacolone enolate.[3a] However, a significant difference between the hexameric pinacolone enolate and the tetrameric enolate exits. This difference is exemplfied by comparing average distances corresponding to C(1)–Li(2) and C(1)–Li(3a) in Figure 3. In the hexamer, the average C(1)–Li(2) distance is only 2.53 Å and the average C(1)–Li(3a) distance is 3.36 Å. For comparison, in the tetramer the average analogous distances are 3.25 and 3.28 Å, respectively. The terminal methylene carbon is ≃0.7 Å closer to one specific lithium atom in the hexameric aggregate. Hence, for the hexameric pinacolone enolate each π bond is paired with a unique lithium atom by virtue of a relatively short distance; whereas in the THF-solvated tetramer, the C-(1)–C(2) σ bond closely bisects a Li–O–Li bond angle and C(1) is more symmetrically disposed with respect to the two staggered lithium atoms.[10]

Calculation of the structure of the "gas-phase" lithium enolate of acetaldehyde at the restricted Hartree–Fock level resulted in three different structures of almost identical minimum energy.[11] A fragment of Figure 3 represented by Li(2)–O(1)–C(2)–C(1) provides experimental realization of one of the calculated enolate geometries with a lithium atom roughly equidistant from both C(1) and C(2). The O–Li bonds are, however, ≃0.23 Å longer in the crystal than in the calculated structure.

The ramifications of this crystal structure for the mechanism of enolate reactions in solution remain to be determined. Evidence for the correlation of X-ray crystal structures of lithiated species with solution species exits.[12] Further investigation to establish this correlation for the hexameric pinacolone enolate as well as crystal structure analyses of additional alkali metal ketone enolates are under way.

Registry No. *tert*-Butyl methyl ketone (lithium enolate), 70367-67-8.

(10) A similarity in both the hexameric and tetrameric enolates is the rather large bond angle of C(2)–O–Li for the one lithium that is approximately anti to C(1) and syn to C(3). Perhaps this is a consequence of the steric bulk of the *tert*-butyl group.

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(12) (a) Bauer, W.; Seebach, D. *Helv. Chim. Acta* **1984,** *67,* 1972. (b) Fraenkel, G.; Henrichs, M.; Su, B. M. *J. Am. Chem. Soc.* **1984,** *106,* 255. (c) Seebach, D.; Gabriel, J.; Hässig, R. *Helv. Chem. Acta* **1984,** *67,* 1083 and previous references in this series. (d) Fraenkel, G.; Pramanik, P. *J. Chem. Soc., Chem. Commun.* **1983,** 1527. (e) Seebach, D.; Hässig, R.; Gabriel *Helv. Chem. Acta* **1983,** *66,* 308. (f) Halaska, V.; Lochmann, L. *Collect. Czech. Chem. Commun.* **1973,** *38,* 1780.

Synthesis, Conformation, and Reactivity of the Rhenium Phosphide Complex (η5-C5H5)Re(NO)(PPh3)(PPh2). The "Gauche Effect" in Transition-Metal Chemistry

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Factors that influence the conformations of metal-bound ligands are fundamentally important and can provide practical insight into reactivity, especially in metal-mediated asymmetric synthesis. Since Corey and Bailar applied concepts from organic conformational analysis to the structures of metal chelate rings over 25 years ago,[1] many steric and electronic contributions to ligand conformations have been identified.[2] We now wish to draw a new, stereoelectronic analogy from organic and main-group element chemistry to transition-metal chemistry—namely, that the "lone pairs" of ligating atoms should prefer to be orthogonal to the metal fragment HOMO.[3] In organic and main-group inorganic compounds, this is commonly called the "gauche effect"[4] and has a profound influence on physical[4,5] and chemical[6] properties.

We first sought evidence for a "gauche effect" in metal phosphide complexes (L_nMPR_2) containing pyramidal phosphorus and hence an unambiguously defined "lone pair".[7] We noted that in Paine's crystal structure of (η5-C5Me5)Fe(CO)2(PN(CH3)-CH2CH2NCH3)[7b] the phosphorus ligand did adopt a conformation in which the lone pair was orthogonal to the iron HOMO. However, the three HOMOs of the (η5-C5H5)Fe(CO)2+ fragment are close in energy.[2b,8] Hence, we synthesized rhenium phosphide complexes (η5-C5H5)Re(NO)(PPh3)(PR2), where the metal fragment HOMO (d orbital shown in 1) would be energetically

(1) Corey, E. J.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1959,** *81,* 2620.

(2) See, inter alia: (a) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975,** *97,* 4292. (b) Faller, J. W.; Johnson, B. V. *J. Organomet. Chem.* **1975,** *96,* 99. (c) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979,** *101,* 585. (d) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *Ibid.* **1979,** *101,* 592. (e) Bushweller, C. H.; Hoogasian, S.; English, A. D.; Miller, J. S.; Lourandos, M. Z. *Inorg. Chem.* **1981,** *20,* 3448. (f) Albright, T. A. *Acc. Chem. Res.* **1982,** *15,* 149. (g) Knowles, W. S. *Ibid.* **1983,** *16,* 106. (h) Seeman, J. I.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1984,** 1019. (i) Baird, M. C., submitted for publication.

(3) We assume a coordinatively saturated metal. Otherwise, bonding can occur between the ligand lone pair and the metal LUMO.

(4) (a) Wolfe, S. *Acc. Chem. Res.* **1972,** *5,* 102. (b) Cowley, A. H.; Mitchell, D. J.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1979,** *101,* 5224. (c) It should be emphasized that n→σ* bonding and other stabilizing interactions contribute to the "gauche effect" in many compounds.

(5) Jolly, W. L. *Acc. Chem. Res.* **1983,** *16,* 370.

(6) See, inter alia: (a) Buncel, E.; Hoz, S. *Tetrahedron Lett.* **1983,** *24,* 4777. (b) DePuy, C. H.; Della, E. W.; Filley, J.; Grabowski, J. J.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1983,** *105,* 2481. (c) Taira, K.; Gorenstein, D. G. *Ibid.* **1984,** *106,* 7825. (d) Taira, K.; Mock, W. L.; Gorenstein, D. G. *Ibid.* **1984,** *106,* 7831. (e) Deslongchamps, P. "Stereoelectronic Effects in Organic Chemistry"; Pergamon Press: New York, 1983.

(7) (a) Barrow, M. J.; Sim, G. A. *J. Chem. Soc., Dalton Trans.* **1975,** 291. (b) Hutchins, L. D.; Duesler, E. N.; Paine, R. T. *Organometallics* **1982,** *1,* 1254. (c) Baker, R. T.; Whitney, J. F.; Wreford, S. S. *Ibid.* **1983,** *2,* 1049. (d) Bohle, D. S.; Jones, T. C.; Rickard, C. E. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1984,** 865. (e) Ebsworth, E. A. V.; Gould, R. O.; McManus, N. T.; Pilkington, N. J.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1984,** 2561.

(8) As a result, two different Fe=CR2 conformations in alkylidene complexes [(η5-C5H5)Fe(L)2(=CR2)]+ have been observed to date: Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *Inorg. Chem.* **1982,** *21,* 1321.

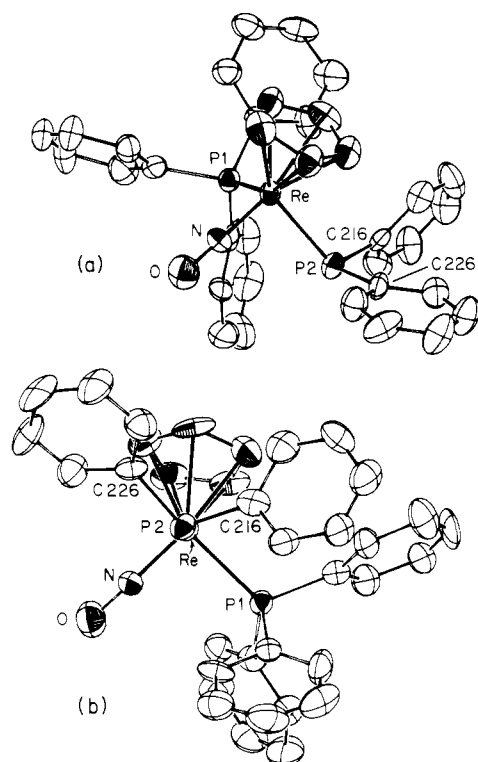**Figure 1.** Two views of the molecular structure of $(\eta^5\text{-}C_5H_5)Re(NO)$-$(PPh_3)(PPh_2)$ (**4**); (b) approximates a Newman projection down the Ph_2P–Re bond. Important bond lengths (Å): Re–P(1), 2.358 (3); Re–P(2), 2.461 (3); Re–N, 1.738 (10); P(2)–C(216), 1.813 (14); P(2)–C-(226), 1.811 (15); N–O, 1.208 (15). Important bond angles (deg): P(1)–Re–P(2), 92.5 (1); P(1)–Re–N, 91.5 (4); P(2)–Re–N, 92.5 (4); Re–P(2)–C(216), 111.7 (5); Re–P(2)–C(226), 107.5 (4); C(226)–P-(2)–C(216), 103.8 (6); Re–N–O, 177.9 (10).

well separated from other occupied orbitals.[9]

Reaction of tosylate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTs)$ (**2**, OTs = $OSO_2\text{-}p\text{-}C_6H_4CH_3$)[10] with PPh_2H (CH_2Cl_2, 25 °C, 2 days) gave $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PPh_2H)]^+$ ^-OTs (**3**, 94%, eq i).[11] Reaction of **3** with t-BuO$^-$ K$^+$ yielded the desired
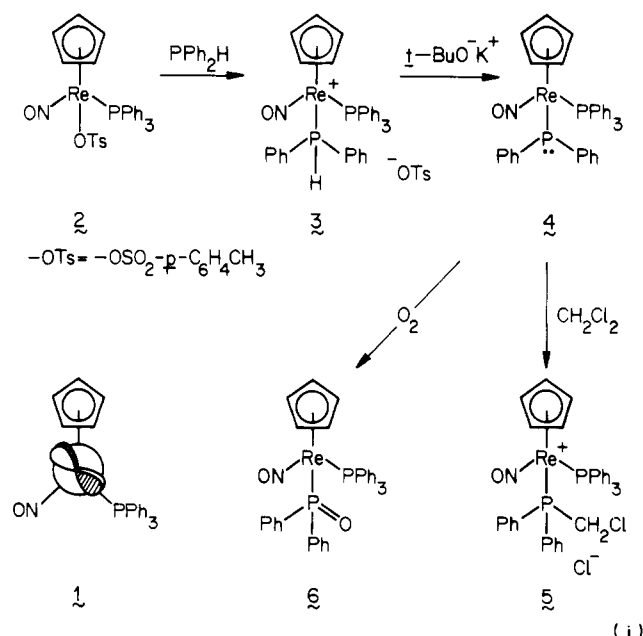
(9) (a) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (b) Georgiou, S.; Gladysz, J. A., unpublished results.
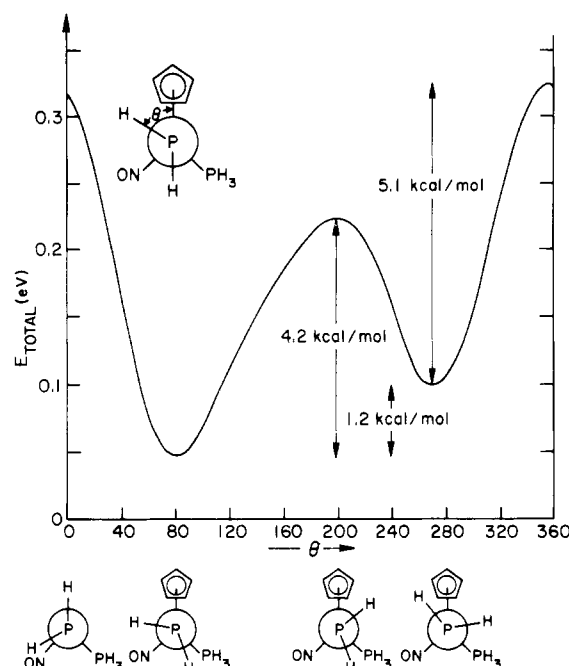(10) Merrifield, J. H.; Fernandez, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

Figure 2. E_{total} for $(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(PH_2)$ as the PH_2 ligand is rotated, calculated ($\geq$1 data point/10°) by the extended Hückel method with weighted H_{ij} formula.

phosphide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PPh_2)$ (**4**, 97%).[11] The X-ray crystal structure of **4** (red crystals from benzene/hexane) was determined as described in the supplementary material.

Two views of the molecular structure of **4**, and important bond lengths and angles, are given in Figure 1. The Re–PPh$_2$ bond (2.461 (3) Å) is significantly longer than the Re–PPh$_3$ bond (2.358 (3) Å). The PPh$_2$ phosphorus is distinctly pyramidal, but the bond angles (107.5°, 111.7°, 103.8°) are markedly greater than usually found in trivalent phosphorus compounds such as PMe$_3$ (99°) and PPh$_3$ (103°).[12] This suggests greater than normal p character in the PPh$_2$ lone pair. The torsion angle between the PPh$_2$ lone pair[13] and the rhenium fragment HOMO (taken as Re–PPh$_3$ bond) is 59.7°, as illustrated by projection b in Figure 1. Hence, the expected near orthogonality of orbitals is observed.

To support our hypothesis that a gauche effect contributes to the conformation of the PPh$_2$ ligand in **4**, extended Hückel MO calculations were conducted on the model compound $(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(PH_2)$. Key results are shown in Figure 2.[14] In contrast to the ~3 kcal, degenerate 3-fold Re–CH$_3$ rotational barrier calculated for $(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(CH_3)$,[9a] $(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(PH_2)$ exhibits a higher, nondegenerate 2-fold Re–PH$_2$ rotational barrier. Energy minima correspond to near-orthogonal orientations of the PH$_2$ lone pair and **1**. One staggered Re–PH$_2$ conformation (θ = 180°), which should be a steric local minimum, is in fact calculated to be almost a local maximum due to eclipsing of the PH$_2$ lone pair and **1**.

Finally, compounds that exhibit the gauche effect often show enhanced solution-phase nucleophilicity ("α effect").[6a–d] Accordingly, **4** and weakly electrophilic CH_2Cl_2[15] readily react (2 h, 25 °C) to give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PPh_2CH_2Cl)]^+$ Cl$^-$

(11) Microanalytical, IR, and NMR (^{1}H, ^{13}C, ^{31}P) data for each new compound are given in the supplementary material.
(12) Corbridge, D. E. C. "The Structural Chemistry of Phosphorus"; Elsevier: New York, 1974; Tables 50 and 51.
(13) The position of the lone pair was determined using the SHELX-76 capability to calculate idealized positions for hydrogen atoms, as described in the supplementary material.
(14) (a) The Re–PH$_2$ distance was set at 2.461 Å, and phosphorus and rhenium were assigned idealized tetrahedral and octahedral geometries, respectively. Other bond lengths and H_{ij} and ζ used were as reported previously.[9a,13b] (b) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.
(15) Alder, R. W.; Baker, R.; Brown, J. M. "Mechanism in Organic Chemistry"; Wiley-Interscience: New York, 1971; p 198.

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J. Am. Chem. Soc. 1985, *107*, 3348–3349

(5, 79%, eq i).[11] Also, 4 is readily oxidized by static air (THF, 21 h) to $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PPh_2O)$ (6, 71%).[11]

In view of the numerous common transition-metal ligands with lone pairs on the ligating atoms (OR, SR, SR$_2$, NR$_2$, etc.), we believe that the ideas set forth above will prove useful in interpreting a large body of structural and reactivity data. Our results also suggest several reasons for the ease of formation and stability of *bridging* phosphide[16] ligands and may bear on the extremely low phosphorus inversion barriers observed with 4 and related complexes.[17]

Supplementary Material Available: Tables of analytical (3–6) and crystallographic (4) data (31 pages). Ordering information is given on any current masthead page.

(16) (a) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163. (b) Schäfer, H. Z. *Anorg. Allg. Chem.* **1980**, *467*, 105. (c) Burckett-St. Laurent, J. C. T. R.; Haines, R. J.; Nolte, C. R.; Steen, N. D. C. T. *Inorg. Chem.* **1980**, *19*, 577. (d) Finke, R. G.; Gaughan, G.; Pierpont, C.; Cass, M. E. *J. Am. Chem. Soc.* **1981**, *103*, 1394. (e) Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *Ibid.* **1983**, *105*, 4826. (f) Kyba, E. P.; Mather, J. D.; Hassett, K. L.; McKennis, J. S.; Davis, R. E. *Ibid.* **1984**, *106*, 5371. (g) Breen, M. J.; Shulman, P. M.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 782. (h) Rosen, R. P.; Hoke, J. B.; Whittle, R. R.; Geoffroy, G. L.; Hutchinson, J. P.; Zubieta, J. A. *Ibid.* **1984**, *3*, 846.

(17) (a) Buhro, W. E.; Gladysz, J. A., submitted for publication. (b) Malisch, W.; Maisch, R.; Meyer, A.; Greissinger, D.; Gross, E.; Colquhoun, I. J.; McFarlane, W. *Phosphorus Sulfur* **1983**, *18*, 299.

An Extremely Short Way to Prostaglandins[1]

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Among various strategies for prostaglandin (PG) synthesis, the three-component coupling process[1] is one of the ideal approaches in view of the directness and synthetic flexibility. Obviously, the ultimate goal along this line is, as illustrated by eq 1 (M = metal, X = halogen), the single-pot construction of the whole frameworks

(1)
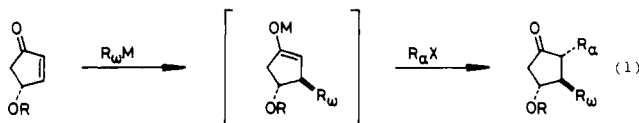
via organometallic-aided conjugate addition of the ω side-chain unit to 4-oxygenated 2-cyclopentenones followed by trapping of the regiochemically defined enolate species by *organic halides* having α side-chain structures. However, Syntex groups[2] among others, after pioneering, extensive study on this possibility, noted extreme difficulty in achieving the direct alkylation.[3] Here we wish to announce the realization of this earnestly desired convergent synthesis. The success relies simply on the lithium (or copper) to tin transmetalation in the enolate stage, a technique elaborated earlier by Tardella (simple alkylation)[4] and Itoh et

(1) Prostaglandin Synthesis. 10. Part 9: Noyori, R.; Suzuki, M. *Angew. Chem.* **1984**, *96*, 854; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 847.

(2) (a) Patterson, J. W., Jr.; Fried, J. H. *J. Org. Chem.* **1974**, *39*, 2506. (b) Davis, R.; Untch, K. G. *Ibid.* **1979**, *44*, 3755.

(3) These papers urged development of some modified or indirect three-component coupling processes. Functionally modified methods: (a) Suzuki, M.; Kawagishi, T.; Suzuki, T.; Noyori, R. *Tetrahedron Lett.* **1982**, *23*, 4057. (b) Suzuki, M.; Kawagishi, T.; Noyori, R. *Ibid.* **1982**, *23*, 5563. (c) Tanaka, T.; Toru, T.; Okamura, N.; Hazato, A.; Sugiura, S.; Manabe, K.; Kurozumi, S.; Suzuki, M.; Kawagishi, T.; Noyori, R. *Ibid.* **1983**, *24*, 4103. (d) Suzuki, M.; Yanagisawa, A.; Noyori, R. *Ibid.* **1984**, *25*, 1383. Indirect methods: Stork, G.; Isobe, M. *J. Am. Chem. Soc.* **1975**, *97*, 6260. Reference 2b. See also: Donaldson, R. E.; Saddler, J. C.; Byrn, S.; McKenzie, A. T.; Fuchs, P. L. *J. Org. Chem.* **1983**, *48*, 2167.

al. (vicinal carba-condensation).[5]

The requisite optically active cyclopentenone and ω side-chain blocks are now accessible in various ways.[1,6] An organocopper reagent was prepared under our standard conditions[7] by mixing the vinyllithium derived from 2a[6,8] in ether and a THF solution containing copper(I) iodide (1 equiv) and tributylphosphine (2.6 equiv). Sequential treatments of the enone 1 with this copper
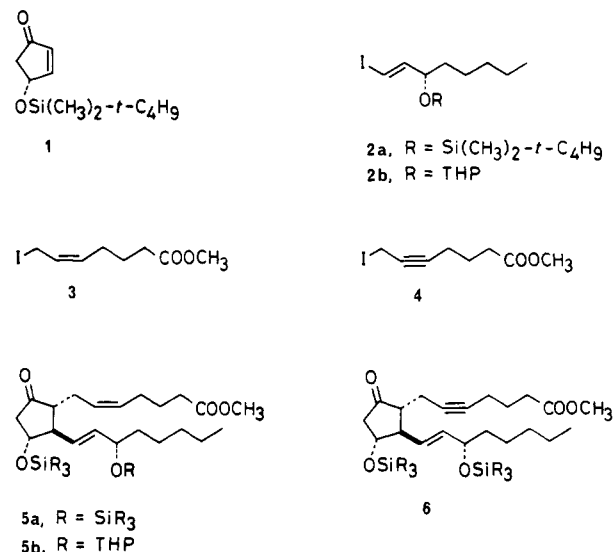
reagent (1:1 molar ratio, −78 °C, 1 h),[9] hexamethylphosphoramide (11 equiv, −78 °C, 30 min), triphenyltin chloride (1 equiv, −78 °C, 10 min), and the allylic iodide 3[10] (5 equiv, −30 to −20 °C, 17 h) afforded stereoselectively the PGE$_2$ derivative 5a in 78% yield,[11–13] $[\alpha]^{19}_D$ −49.9° (c 1.02, CH$_3$OH). No PGA derivatives were detected. Natural PGE$_2$ can be obtained from 5a by removal of the silyl protective group with HF–pyridine[3b] followed by enzymatic ester hydrolysis.[14] In a like manner, 5b (a versatile precursor of D series of PGs), $[\alpha]^{16}_D$ −60.0° (c 1.02, CH$_3$OH), was prepared in 77% yield by the one-pot condensation of 1, 2b, and 3.[13] Use of methyl 7-iodoheptanoate, a saturated alkylating agent (−20 °C, 16 h), gave the corresponding PGE$_1$ derivative in only 20% yield.[13]

Utilization of the propargylic iodide[15] as the α side-chain unit allowed the synthesis of 6 in 82% yield, $[\alpha]^{17}_D$ −13.2° (c 0.59,

(4) Tardella, P. A. *Tetrahedron Lett.* **1969**, 1117. See also: Yamamoto, Y.; Maruyama, K. "Abstract of Papers"; 28th Symposium on Organometallic Chemistry, Japan, Osaka, Nov 1981; p 151.

(5) Nishiyama, H.; Sakuta, K.; Itoh, K. *Tetrahedron Lett.* **1984**, *25*, 223; **1984**, *25*, 2487.

(6) In this context, asymmetric reduction with the binaphthol-modified lithium aluminum hydride reagent is very useful: Noyori, R.; Tomino, I.; Yamada, M.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6717.

(7) Suzuki, M.; Suzuki, T.; Kawagishi, T.; Morita, Y.; Noyori, R. *Isr. J. Chem.* **1984**, *24*, 118.

(8) For optical resolution of the ω side-chain unit, see: Kluge, A. F.; Untch, K. G.; Fried, J. H. *J. Am. Chem. Soc.* **1972**, *94*, 7827.

(9) The conjugate addition proceeds in a completely stereoselective manner to give after aqueous quenching only the C-11/C-12 (PG numbering) trans product.[1]

(10) Posner, G. H.; Sterling, J. J.; Whitten, C. E.; Lentz, C. M.; Brunelle, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 107.

(11) In model vicinal carba-condensation procedures, tributyltin chloride,[4,5] iodide, or fluoride (but not triflate) could also be used, but less effectively. We consider that the alkylation proceeds via the penta- or hexacoordinate stannate species. For alkylation of tin(IV) enolates and related species, see: Odic, Y.; Pereyre, M. *J. Organomet. Chem.* **1973**, *55*, 273. References 4 and 5.

(12) In addition, the C-8 epimer[13] was obtained in 2–3% yield.

(13) All products were identified by comparison with authentic samples.

(14) Sih, C. J.; Heather, J. B.; Sood, R.; Price, P.; Perzzotti, G.; Lee, L. F. H.; Lee, S. S. *J. Am. Chem. Soc.* **1975**, *97*, 865. Hazato, A.; Tanaka, T.; Toru, T.; Okamura, N.; Bannai, K.; Sugiura, S.; Kurozumi, S. *Nippon Kagaku Kaishi* **1983**, 1392.

(15) Prepared by treatment of 6-(carbomethoxy)-2-hexyn-1-ol with a mixture of triphenyl phosphite, iodine, and pyridine (3 equiv each) in ether (0 °C, 30 min) in 73% yield.