

New Ligands with a Wide Bite Angle. Efficient Catalytic Activity
in the Rh(I)-Catalyzed Hydroformylation of Olefins

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The relevance of a new diphosphinite, which holds a natural bite angle around 120° in a catalyst complex, to the Rh(I)-catalyzed hydroformylation of certain olefins is examined, exhibiting a high turnover frequency (TOF) as compared with a typical 1,2-bis(diphenylphosphino)ethane with a bite angle around 85°.

Homogeneous hydroformylation of terminal olefins catalyzed by Rh(I) complexes with supporting triphenylphosphine ligands is known that more desirable pathway to linear aldehyde over a branched one is enhanced by an excess phosphine and lowered pressures of CO at the expense of reaction rate.¹⁾ Much effort has been directed towards the asymmetric hydroformylation using conventional optically active diphosphine ligands in 1970s, scarcely succeeding in a Rh(I) catalyst system but in Pt(II)/SnCl₂ systems.²⁾ A recent communication³⁾ on the highly enantioselective hydroformylation catalyzed by new phosphinephosphite-Rh(I) complexes prompted us to report here our own line of research in a preliminary form. Based on a widely accepted mechanism for the phosphine-Rh(I)-catalyzed hydroformylation of terminal olefins, it seems reasonable to expect that, under a H₂-CO pressure, ubiquitous trigonal bipyramidal Rh(I) complexes with a favorable diequatorial chelation of a given diphosphine or diphosphinite, which holds a natural bite angle around 120°, play presumably a crucial role in the catalytic loop.⁴⁾ Thus, understanding how to "fine tune" the ligand effects to make catalyst systems more active and more selective is a major concern of our present work.

We have already prepared (1*R**,2*R**,4*R**,5*R**)-2,5-bis(diphenylphosphinomethyl)bicyclo[2.2.1]heptane (**1**), which is unique in holding a calculated (CACHe) bite angle of 123° as well as a C₂ axis of symmetry.⁵⁾ Treatment of Rh(nbd)(acac), 42% HBF₄, and an equimolar amount of **1** in THF under argon at room temperature afforded a monomeric [Rh(nbd)(**1**)]⁺BF₄⁻ along with a dimer complex bridged by **1**. The latter was sparingly soluble in CHCl₃ and readily separated by centrifugation: ³¹P NMR (202 MHz, CD₂Cl₂), monomer δ 20.2 (d, *J* = 146 Hz), dimer δ 19.2 ppm (d, *J* = 146 Hz).⁶⁾ It is worth mentioning that the monomer is, in fact, a major product even though it is highly constrained within a square planar geometry, while the dimer must be free from such a strain but suffering from steric congestion. The monomeric, cationic Rh(I) was used as a catalyst precursor (0.5 mol%) for the regioselective hydroformylation of styrene and vinylarenes under mild conditions (CO/H₂, 20-40 atm, 25-50 °C) to give high branch/linear ratios of up to 97/3.⁵⁾ Being encouraged by these results, we have prepared a new diphosphinite, (1*R**,2*R**,4*R**,5*R**)-2,5-bis(diphenylphosphinoxy)bicyclo[2.2.1]heptane (**2**),⁷⁾ which has a bite angle of 118° (CACHe) and is probably a little more flexible than diphosphine **1** as shown in Fig. 1.⁵⁾

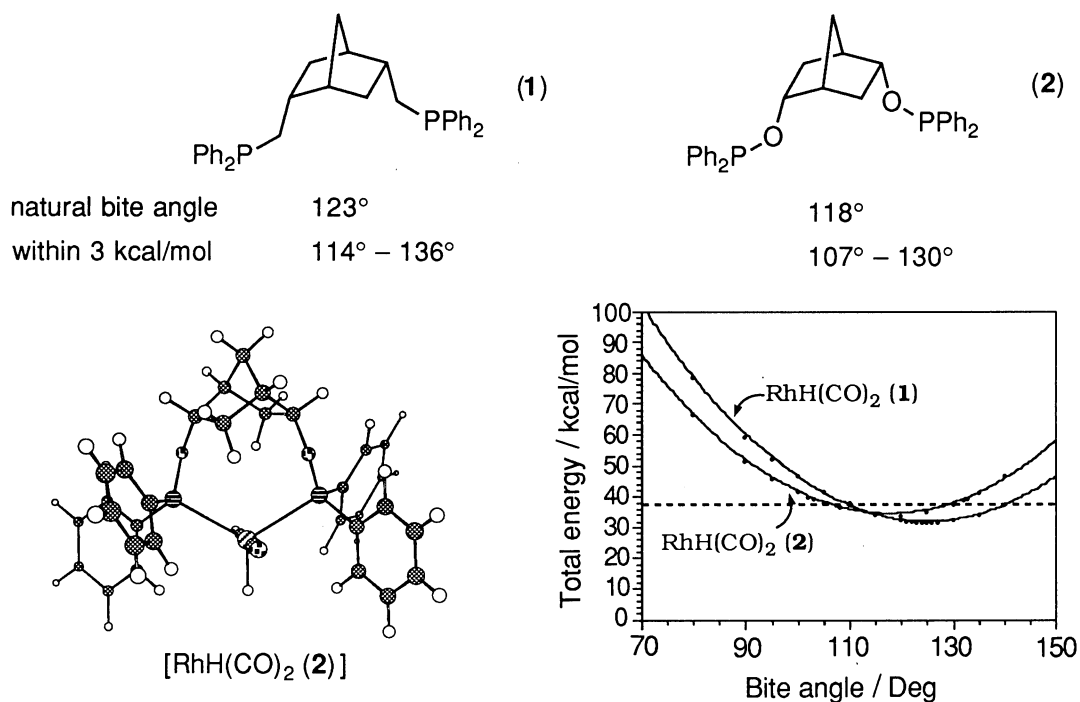
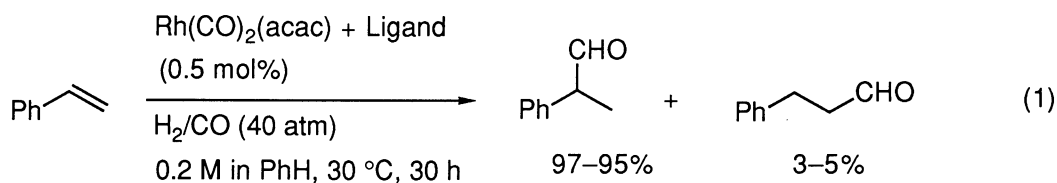
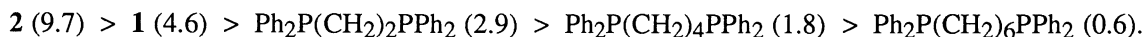


Fig. 1. Bite angles by CAChe calculations.

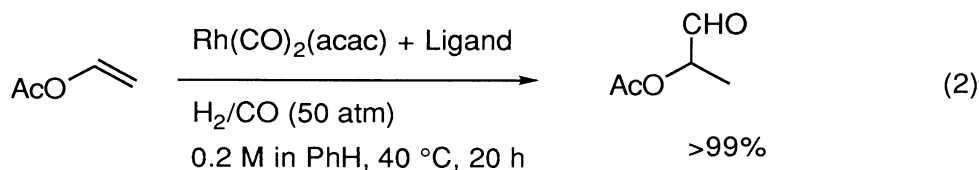
Regioselective hydroformylation of styrene (2-phenylpropanal was obtained in up to 97% selectivity) catalyzed by $[\text{Rh}(\text{CO})_2(\text{acac}) + \text{1 or 2}]$ (0.5 mol%; $\text{Rh}/\text{ligand} = 1.2$) under $\text{H}_2 + \text{CO}$ (1/1, 40 atm) at 30 °C for 30 h in a benzene solution (initial concentration 0.2 M) was carried out (Eq. 1). For comparison purposes, 1,2-



bis(diphenylphosphino)ethane, 1,4-bis(diphenylphosphino)butane, and 1,6-bis(diphenylphosphino)hexane, respectively, were also used for the hydroformylation of styrene instead of the new ligands **1** or **2** under exactly the same conditions as above. It was thus found that the catalytic efficiency in terms of the turnover frequency (TOF; $\text{Rh atom}^{-1} \cdot \text{h}^{-1}$ at 30 °C) was in the order



Essentially the same order as above was observed in the completely regioselective hydroformylation of vinyl acetate using the same catalyst systems (Eq. 2). TOF: **2** (9.6) > **1** (4.2) > $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ (2.1).

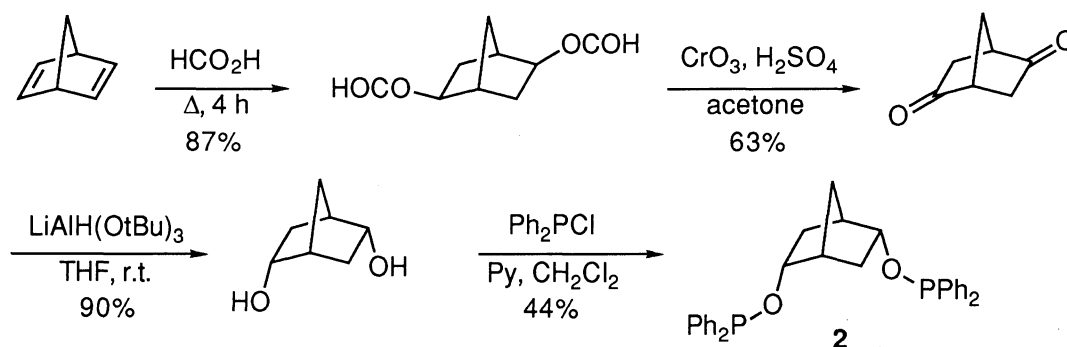


It is emphasized that the observed TOF (9.7) for a Rh(I) catalyst with diphosphinite **2** well rivals the TOF (8) for $\text{Rh}_4(\text{CO})_{12}$ -catalyzed hydroformylation of *t*-butylethylene in hexane under the mildest conditions ($\text{H}_2/\text{CO} = 1/1$, 20 atm, at 20 °C).⁸⁾ Consequently, the new ligand **2** appears not to retard significantly the overall rate of hydroformylation of certain terminal olefins, though valid structural elucidation for $[\text{RhH}(\text{CO})_2(\text{2})]^{4)}$ must be done. We have also prepared optically pure **1**⁹⁾ and **2**,¹⁰⁾ respectively. However, none of these are effective to induce significant asymmetry in the aldehyde products represented in equations 1 and 2. Modification of **2** is now underway.

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References

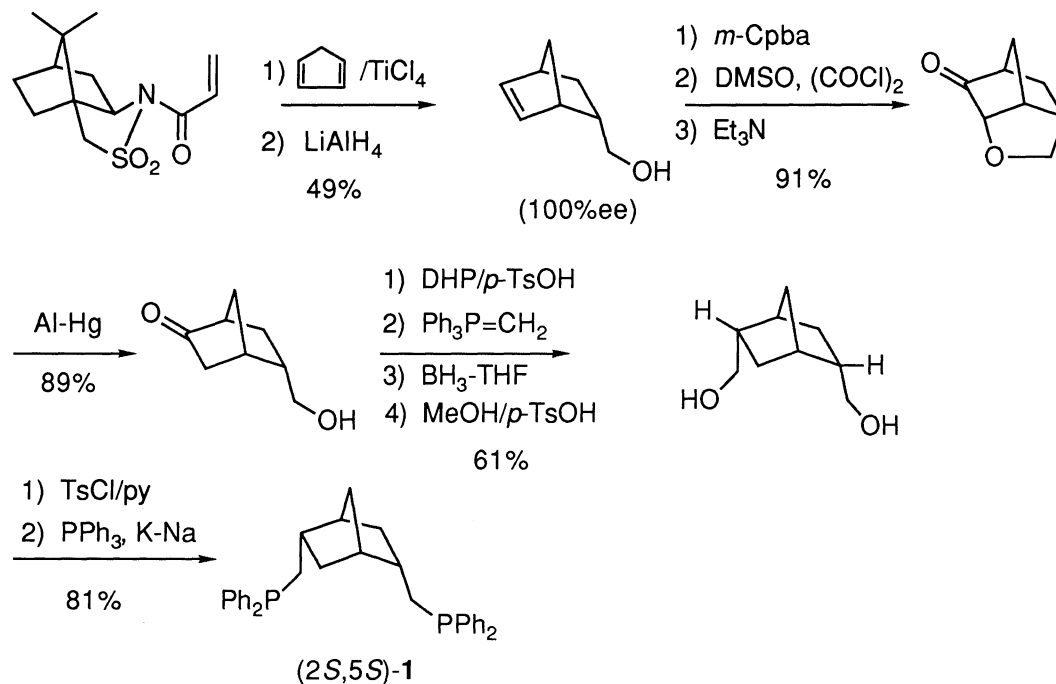
- 1) C.A. Tolman and J. W. Faller, "Homogeneous Catalysis with Metal Phosphine Complex," ed by L. H. Pignolet, Plenum Press, New York (1983), Chap. 2, pp. 81ff.
- 2) I. Ojima and K. Hirai, "Asymmetric Synthesis," ed by J. D. Morrison, Academic Press, New York (1985), Vol. 5, Chap. 4, pp.126-139.
- 3) N. Sakai, S. Mano, K. Nozaki, and H. Takaya, *J. Am. Chem. Soc.*, **115**, 7033 (1993).
- 4) A relevant complex with triphenylphosphine, $\text{HRh}(\text{CO})_2(\text{PPh}_3)_2$, has been shown to consist of an 85% diequatorial isomer and of 15% apical-equatorial one: J. M. Brown and A. G. Kent, *J. Chem. Soc., Perkin Trans. 2*, **1987**, 1597.
- 5) M. Miyazawa, S. Momose, and K. Yamamoto, *Synlett*, **1990**, 711. The natural bite angle has been calculated for a (diphosphine)Rh fragment based on a Rh-P bond length of 2.30 Å: C. P. Casey and G. T. Whiteker, *Isr. J. Chem.*, **30**, 299 (1990). However, the present CAChe calculations were performed on the particular complex shown in Fig. 1.
- 6) M. Funahashi, MS Thesis, Tokyo Institute of Technology (1993), Chap. 2; manuscript submitted for publication.
- 7) Procedure for the preparation of ($\pm$)-**2** is depicted in Scheme 1. Spectral data of **2** given: ^1H NMR (270 MHz, CDCl_3) δ 1.37 (brs, 2H), 1.75 (ddd, $J = 4.6, 11.9, 13.5$ Hz, 2H), 2.00 (d, $J = 13.5$ Hz, 2H), 2.33 (brs, 2H), 4.41 (m, 2H), 7.2-7.6 ppm (m, 20H). ^{13}C NMR (125 MHz, CDCl_3) δ 29.2 (d, $J = 6.1$ Hz), 35.3 (d, $J = 6.1$ Hz), 42.2 (d, $J = 4.9$ Hz), 80.7 (d, $J = 18.4$ Hz), 128.1 (d, $J = 7.3$ Hz), 128.9 (d, 18.3 Hz), 129.9 (d, $J = 21.9$ Hz), and 130.4 ppm (d, $J = 23.1$ Hz).



Scheme 1.

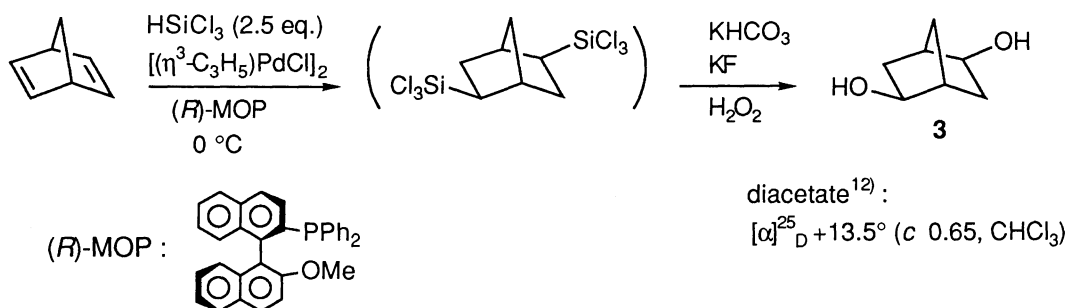
8) M. Garland (E.T.H.), private communication.

9) Procedure for the preparation of (1*S*,2*S*,4*S*,5*S*)-**1** is depicted in Scheme 2. Spectral and rotation data of **1** given: ^{31}P NMR (202 MHz, CDCl_3) -17.8 ppm: $[\alpha]^{25}_{\text{D}} +27.6^\circ$ (*c* 0.70, CHCl_3): mp 84-85 °C.



Scheme 2.

10) According to the asymmetric hydrosilylation of norbornadiene followed by oxidative cleavage of the resulting disilylated norbornane derivative (Scheme 3),¹¹⁾ optically pure (1*R*,2*S*,4*R*,5*S*)-norbornanediol (**3**) was prepared. By exactly the same procedure as that given in Scheme 1 was obtained optically pure (1*R*,2*R*,4*R*,5*R*)-**2**, $[\alpha]^{25}_{\text{D}} +23.3^\circ$ (*c* 2.4, CHCl_3).



Scheme 3.

11) Y. Uozumi, S.-Y. Lee, and T. Hayashi, *Tetrahedron Lett.*, **33**, 7185 (1992).

12) K. Naemura, N. Takahashi, H. Ida, and S. Tanaka, *Chem. Lett.*, **1991**, 657.

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