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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)/$SnCl_2$ 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 H_2-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 C_2 axis of symmetry.5) Treatment of Rh(nbd)(acac), 42% HBF_4, and an equimolar amount of **1** in THF under argon at room temperature afforded a monomeric $[Rh(nbd)(\mathbf{1})]^+BF_4^-$ along with a dimer complex bridged by **1**. The latter was sparingly soluble in $CHCl_3$ and readily separated by centrifugation: ^{31}P NMR (202 MHz, CD_2Cl_2), 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/H_2, 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)

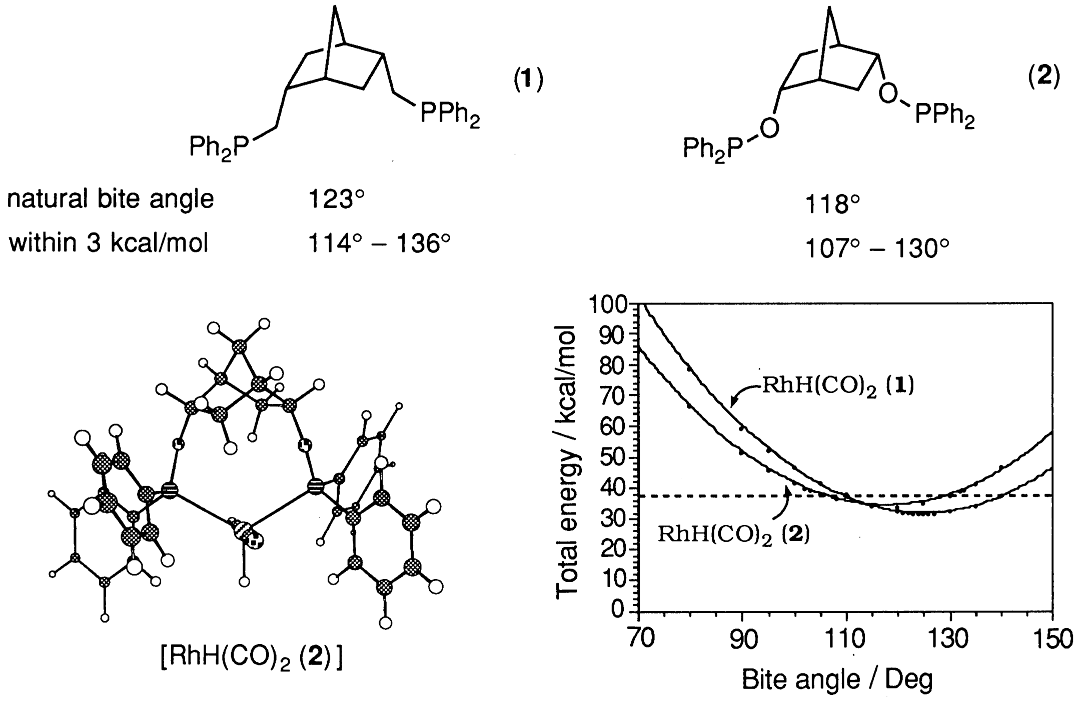
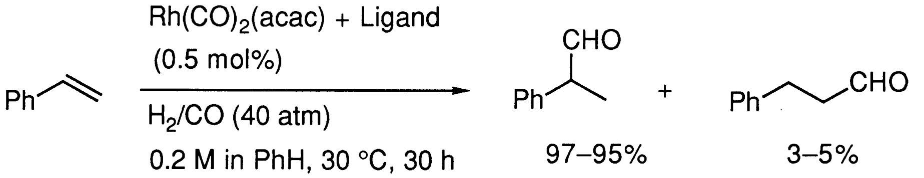


Fig. 1. Bite angles by CAChe calculations.

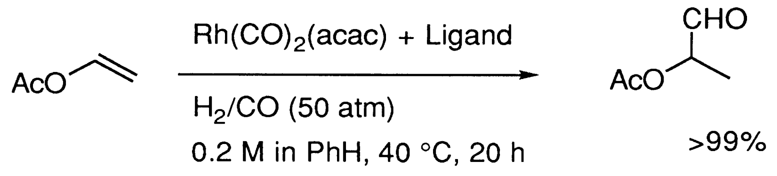
Regioselective hydroformylation of styrene (2-phenylpropanal was obtained in up to 97% selectivity) catalyzed by [$Rh(CO)_2(acac)$ + **1** or **2**] (0.5 mol%; Rh/ligand = 1.2) under H_2 + CO (1/1, 40 atm) at 30 °C for 30 h in a benzene solution (initial concentration 0.2 M) was carried out (Eq. 1). 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; Rh $atom^{-1}{\bullet}h^{-1}$ at 30 °C) was in the order



(1)

2 (9.7) > **1** (4.6) > $Ph_2P(CH_2)_2PPh_2$ (2.9) > $Ph_2P(CH_2)_4PPh_2$ (1.8) > $Ph_2P(CH_2)_6PPh_2$ (0.6).

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) > $Ph_2P(CH_2)_2PPh_2$ (2.1).



(2)

It is emphasized that the observed TOF (9.7) for a Rh(I) catalyst with diphosphinite **2** well rivals the TOF (8) for $Rh_4(CO)_{12}$-catalyzed hydroformylation of *t*-butylethylene in hexane under the mildest conditions (H_2/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 $[RhH(CO)_2$ (**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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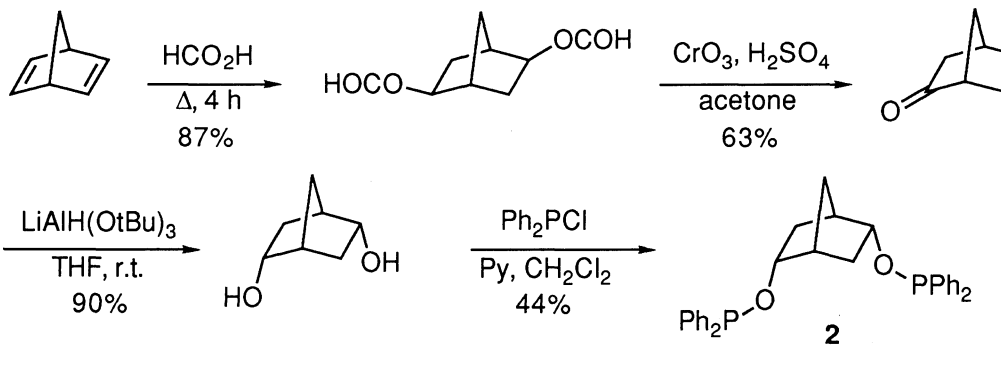
References

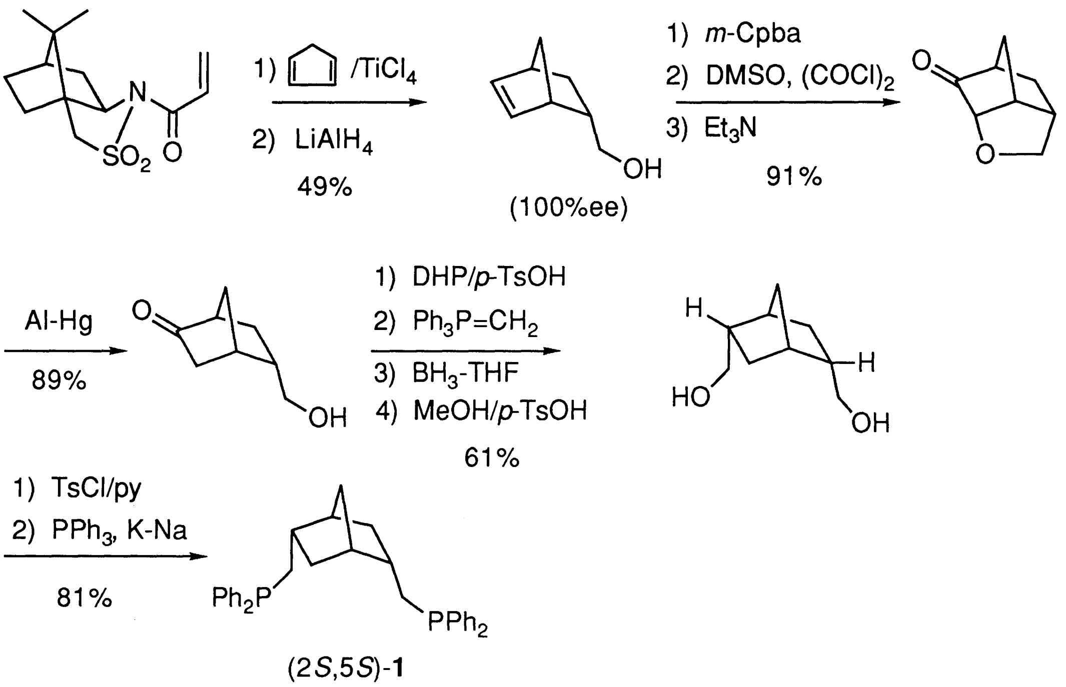
1) C.A. Tolman and J. W. Faller, "Homogeneous Catalysis with Metal Phosphine Complex," ed by L. H. Pignolet, Plenum Press, New York (1983), Chap. 2, pp. 81ff.
2) I. Ojima and K. Hirai, "Asymmetric Synthesis," ed by J. D. Morrison, Academic Press, New York (1985), Vol. 5, Chap. 4, pp.126-139.
3) N. Sakai, S. Mano, K. Nozaki, and H. Takaya, *J. Am. Chem. Soc.*, **115**, 7033 (1993).
4) A relevant complex with triphenylphosphine, $HRh(CO)_2(PPh_3)_2$, 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 (±)-**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.

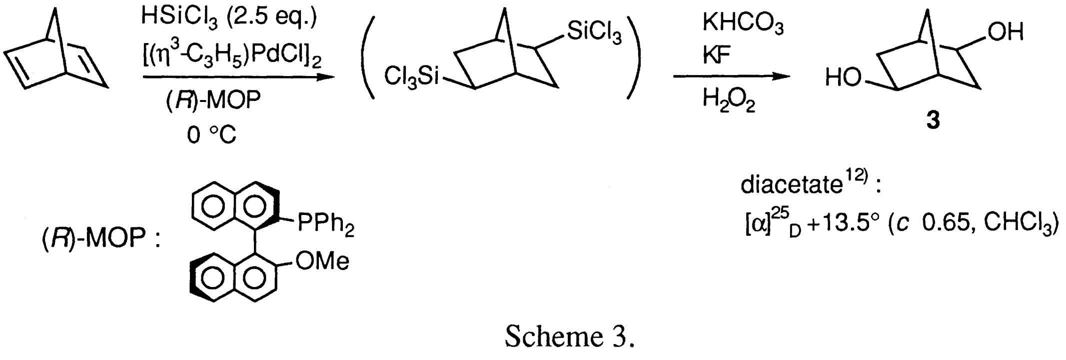
8) M. Garland (E.T.H.), private communication.

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 : $[\alpha]^{25}_D$ +27.6° (*c* 0.70, $CHCl_3$): mp 84-85 °C.



Scheme 2.

10) According to the asymmetric hydrosilation 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**, $[\alpha]^{25}_D$ +23.3° (*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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