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FULLY ALKYLATED CHIRAL DIPHOSPHINES, RDIOP, AND THEIR Rh(I) COMPLEXES

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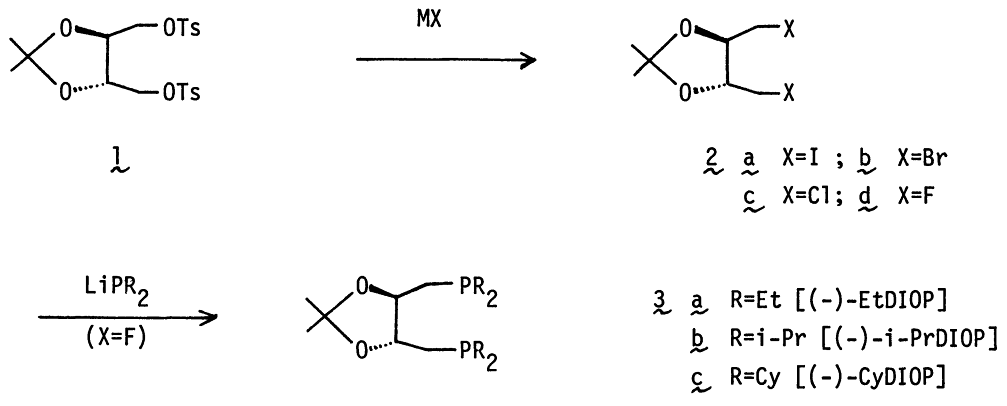
Tetraalkyl analogs of DIOP, (-)-EtDIOP, (-)-i-PrDIOP, and (-)-CyDIOP, have been prepared for the first time by the reaction of (+)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-difluorobutane and the corresponding lithium dialkylphosphides. These diphosphines form cationic Rh(I) complexes, [Rh{(-)-RDIOP}(NBD)]ClO_4 (R=Et, i-Pr, and Cy), which show remarkable reactivity toward dihydrogen.

Rhodium(I) complexes of a variety of optically active chelating diphosphines or aminophosphines have been proposed as asymmetric hydrogenation catalysts.[1)] All the chiral diphosphines or aminophosphines reported so far have at least one aromatic substituent on the phosphorus atom, and their rhodium(I) complexes are less active for the hydrogenation of ketones than for olefins. Although high optical yields have been obtained in the production of chiral alcohols with some of these complex catalysts[2)], the catalytic rates were very slow under ambient conditions employing atmospheric pressure of hydrogen. Recently we prepared cationic Rh(I) complexes of a cis-chelate alkyldiphosphine, [Rh{$(i\text{-}Pr)_2P(CH_2)_nP(i\text{-}Pr)_2$}(NBD)]$ClO_4$ (n=3,4; NBD=norbornadiene) which show excellent catalytic activity for the hydrogenation of carbonyl compounds.[3)] This finding led us to synthesize chiral diphosphines with similar electronic properties. Among the ligands frequently used for asymmetric catalysis is DIOP [2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane].[1)] This chiral, tetraaryldiphosphine is readily prepared from the natural product tartaric acid.[4)] Replacement of the aryl substituents with alkyl groups has not hitherto been reported. In this paper we wish to describe the first successful synthesis of the tetraalkyl analogs, RDIOP, and their cationic Rh(I) complexes, which are expected to be highly active for ketone hydrogenation.

An obvious route to RDIOP, is through the conventional nucleophilic substitution reaction of the ditosylate **1**. The reaction of **1** with alkali metal dialkylphosphide, however, produced only untractable substances. Since fully alkylated diphosphines, $R_2P(CH_2)_nPR_2$ (n=3,4) can be prepared by reacting $X(CH_2)_nX$ with R_2PLi,[5)] the reactions of the dihalides (**2a**-**c**), with R_2PLi were studied under various conditions. The reactions produced mainly diphosphane, R_2PPR_2, and unidentifiable products, only a very small amount of the desired diphosphine **3** being formed. However, to our surprise, **3** could be isolated in substantial yields from the reaction of the difluoride **2d** with R_2PLi.



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2 **a** X=I ; **b** X=Br
c X=Cl; **d** X=F

3 **a** R=Et [(-)-EtDIOP]
b R=i-Pr [(-)-i-PrDIOP]
c R=Cy [(-)-CyDIOP]

The key substance, (+)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-difluorobutane, **2d**, was obtained in 63% yield by heating (130°C/11-12 Torr) the ditosylate **1** with an excess of anhydrous potassium fluoride in absolute diethylene glycol. It is a colorless liquid[6], bp 56-57°C/16 Torr, $[\alpha]_D^{25}$ + 23.4° ($CHCl_3$, c1.64); ^1H-NMR($CDCl_3$) δ1.45 (s, 6H, $C\underline{H}_3$), 4.13 (m, 2H, -C$\underline{H}$-), 4.50 (dd, J_{HH}=3.5Hz, J_{HF}=49Hz, 4H, $C\underline{H}_2F$); ^{19}F-NMR($CDCl_3$) (upfield from C_6F_6) δ68.0 (dt, $^2J_{HF}$=49Hz, $^3J_{HF}$=21Hz). The reaction of the difluoride, **2d** (20 mmol) with R_2PLi (60 mmol) in dioxane or a dioxane-THF mixture proceeds smoothly at ambient temparature to give the expected optically active alkyldiphosphine **3** as an air-sensitive colorless liquid [(-)-EtDIOP and (-)-i-PrDIOP] or solid [(-)-CyDIOP] in practical yields. These air-sensitive phosphines can be purified by vacuum distillation or recrystallization and characterized spectroscopically (Table 1). More conveniently, however, the purification can be carried out by recrystallization of their air-stable solid CS_2-adduct, especially in the case of (-)-CyDIOP.[7] The free diphosphine is readily and quantitatively recovered from the CS_2-adduct by simply heating in refluxing EtOH under nitrogen.

Cationic Rh(I) complexes of (-)-RDIOP can be prepared following the conventional method. Namely, [Rh{(-)-RDIOP}(NBD)]ClO_4 (**4**) was obtained by treating $[Rh(NBD)_2]ClO_4$, prepared in situ from $[Rh(NBD)Cl]_2$, NBD, and $AgClO_4$, with (-)-RDIOP in acetone or methanol at ambient temperature. Recrystallization of the complexes from acetone-ether gave crystalline products. These complexes were fully characterized from their IR, ^1H- and ^{31}P-NMR, and elemental analysis (Table 2).[8]

One of the remarkable properties of these Rh(I) complexes is their high affinity toward dihydrogen. Thus a facile addition of H_2 to e.g. [Rh{(-)-CyDIOP}(NBD)]ClO_4, (ambient temperature, 1 atm) takes place to give a cis-dihydridorhodium adduct [Rh{(-)-CyDIOP}H_2]ClO_4 as yellow crystals[9], mp 148-150°C (under N_2), IR(nujol) 2100 and 2075cm^{-1} for Rh-H; ^1H-NMR(CD_2Cl_2) δ -8.2 (br) and -19.8 ppm (br) for hydride signals. This successful isolation of a cationic cis-chelating diphosphine dihydridorhodium complex is unprecedented. Similar cationic Rh(I) complexes of conventional

Table 1. Properties of (-)-RDIOP

(-)-RDIOP	Reaction Condition	Yield (%)	bp(°C/Torr) [mp(°C)]	$[\alpha]_D^{20}$(°)	^{1}H-NMR ($CDCl_3$)
3a R=Et	r.t./dioxane 22h	83	90-91/10^{-3}	-25.5($CHCl_3$, c6.63)	δ1.06(dt, J_{PH}=14Hz, J_{HH}=5Hz, 12H, $CH_2C\underline{H}_3$), 1.38[s, 6H, $(C\underline{H}_3)_2C<$], 1.42(m, 8H, $C\underline{H}_2$-CH_3), 1.70(m, 4H, $C\underline{H}_2P$), 3.86ppm(m, 2H, -C$\underline{H}$O-)
3b R=i-Pr	r.t./dioxane -THF(1:1) 22h	34	125-130/10^{-3}	-31.0(C_6H_6, c2.97)	δ1.30[m, 24H, $(C\underline{H}_3)_2CH$], [a] 1.37[s, 6H, $(C\underline{H}_3)_2C<$], 2.10 (m, 8H, C$\underline{H}$ + $C\underline{H}_2P$), 4.23ppm (m, 2H, -C$\underline{H}$O-)
3c R=Cy	35°/dioxane 42h	74	[90-92]	-24.1(C_6H_6, c0.97)	δ1.24 and 1.80(br, 48H, Cy + $C\underline{H}_2P$), 1.42[s, 6H, $(C\underline{H}_3)_2C<$], 3.81ppm(m, 1H, -C$\underline{H}$O-)

a) Measured as disulfide.

Table 2. Properties of [Rh{(-)-RDIOP}(NBD)]ClO_4

Complex	RDIOP	Yield(%)	Color	mp(dec)°C	^{31}P-NMR[a] ($CDCl_3$)	^{1}H-NMR ($CDCl_3$)
4a	EtDIOP	72	red	124	δ 6.4ppm (d,J=150Hz)	δ0.9 – 1.5(m, 12H, $C\underline{H}_3$), 1.41(s, 6H, $C\underline{H}_3$), 1.76(6r s, 2H, $C\underline{H}_2$ of NBD), 1.80 – 2.70(br, 12H, $C\underline{H}_2$), 3.82(br, 2H, -C$\underline{H}$O-), 4.15(br s, 2H, C$\underline{H}$ of NBD), 5.14ppm(m, 4H, C$\underline{H}$=)
4b	i-PrDIOP	69	red	145	δ22.3ppm (d,J=152Hz)	δ1.00 – 1.56(m, 24H, $C\underline{H}_3$), 1.42(s, 6H, $C\underline{H}_3$), 1.80(br s, 2H, $C\underline{H}_2$ of NBD), 2.0 – 2.8(br, 8H, C$\underline{H}$ + $C\underline{H}_2$), 3.76(br, 2H, -C$\underline{H}$O-), 4.12(br s, 2H, C$\underline{H}$ of NBD), 5.02ppm(m, 4H, C$\underline{H}$=)
4c	CyDIOP	86	orange	182	δ16.5ppm (d,J=151Hz)	δ1.00– 3.0(complex signal, 48H, Cy + $C\underline{H}_2$), 1.43(s, 6H, $C\underline{H}_3$), 3.79(br, 2H, -C$\underline{H}$O-), 4.12(br s, 2H, C$\underline{H}$ of NBD), 4.79(br s, 2H C$\underline{H}$=), 4.92ppm(br s, 2H, C$\underline{H}$=)

a) Downfield from external H_3PO_4.

cis-chelating aryldiphosphines such as bis(diphenylphosphino)ethane[10], DIOP[11,12], DIPAMP[11,12], Chiraphos[11,12], etc., fail to give the corresponding *cis*-dihydride species. The complexes **4** proved to be highly active catalysts for asymmetric hydrogenation of ketones, as will be described separately.

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References

1) a) D. Valentine, Jr., and J. W. Scott, Synthesis, 1978, 329.
   b) H. B. Kagan and J. C. Fiaud, "Topics in Stereochemistry," ed. by E. L. Eliel and N. L. Allinger, Wiley-Interscience, New York (1978), Vol. 10, p. 175.
   c) R. Pearce, Catalysis, 2, 176 (1978).
   d) B. Bosnich and M. D. Fryzuk, "Topics in Inorganic and Organometallic Stereochemistry," ed. by G. Geoffroy, Wiley-Interscience, New York (1981), p. 119.
2) a) T. Hayashi, T. Mise, and M. Kumada, Tetrahedron Lett., 1976, 4351.
   b) I. Ojima, T. Kogure, T. Terasaki, and K. Achiwa, J. Org. Chem., 43, 3444 (1978).
   c) I. Ojima and T. Kogure, J. Organomet. Chem., 195, 239 (1980).
   d) T. Hayashi, A. Katsumura, M. Konishi, and M. Kumada, Tetrahedron Lett., 1979, 425.
   e) S. Törös, B. Heil, L. Kollár, and L. Markó, J. Organomet. Chem., 197, 85 (1980).
3) K. Tani, K. Suwa, E. Tanigawa, T. Yoshida, T. Okano, and S. Otsuka, Chem. Lett. (1982) in press.
4) H. B. Kagan and T.-P. Dang, J. Am. Chem. Soc., 94, 6429 (1972).
5) K. Issleib and D.-W. Müller, Chem. Ber., 92, 3175 (1959).
6) *Anal* Found: C, 50.78; H, 7.42%. Calcd for $C_7H_{12}F_2O_2$: C, 50.60; H, 7.28%.
7) mp 107°C(dec). *Anal* Found: C, 58.67; H, 8.32%. Calcd for $C_{33}H_{56}O_2P_2S_4$: C, 58.72; H, 8.36%.
8) Elemental analysis: **4a**, Found: C, 43.37; H, 6.55%. Calcd for $C_{22}H_{40}ClO_6P_2Rh$: C, 43.98; H, 6.71%. **4b**, Found: C, 46.92; H, 7.31%. Calcd for $C_{26}H_{48}ClO_6P_2Rh$: C, 47.53; H, 7.36%. **4c**, Found: C, 55.33; H, 7.86%. Calcd for $C_{38}H_{64}ClO_6P_2Rh$: C, 55.85; H, 7.89%.
9) The exact structure of the dihydride is not clear at the moment. Further study on the dihydride is now in progress.
10) J. Halpern, D. P. Riley, A. C. S. Chan, and J. J. Pluth, J. Am. Chem. Soc., 99, 8055 (1977).
11) D. A. Slack, I. Greveling, and M. C. Baird, Inorg. Chem., 18, 3125 (1979).
12) J. M. Brown, P. A. Chaloner, A. G. Kent, B. A. Murrer, P. N. Nicholson, D. Parker, and P. J. Sidebottom, J. Organomet. Chem., 216, 263 (1981).

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