New chiral chelating phosphine complexes containing tricarbonyl(η⁶-arene) chromium for highly enantioselective allylic alkylation

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Received 1 February 1995; in revised form 15 March 1995

Abstract

New chiral phosphine complexes with an additional chelating group containing tricarbonyl(η^6-arene)chromium were prepared from (R)-1-phenylethylamine and (S)-1-phenylethanol. Catalytic asymmetric allylic alkylation of 1,3-diphenyl-1-acetoxypropene with sodium dimethyl malonate in the presence of palladium(0) catalyst with the chiral (arene)chromium complexes gave the alkylation product of up to 94% ee.

Keywords: (Arene)chromium; Chiral phosphine ligand; Planar chirality; Catalysis; Allylic alkylation

1. Introduction

There has been great interest in the asymmetric synthesis catalyzed by chiral phosphine–transition metal complexes [1], and the preparation of the chiral phosphine ligands which are capable of bringing about high enantioselectivity is essential for a development of the catalytic asymmetric synthesis. The use of the (arene)chromium complexes as the chiral ligands is scarce in the catalytic asymmetric reactions [2], while the ferrocenyl complexes have been proven to be highly enantioselective ligands for a variety of catalytic asymmetric reactions [3]. We have recently reported that some chiral (arene)chromium complexes derived from (R)-tricarbonyl(N,N-dimethyl-1-phenylethylamine)-chromium can be utilized for the catalytic asymmetric reactions; thus we have the asymmetric cross-coupling reaction of 1-phenylethyl metals with vinyl bromides utilizing the amino-phosphine ligands [2c], and the asymmetric ethylation of benzaldehyde catalyzed by the chiral amino-alcohol ligands containing arene–chromium complexes [2a,b]. These chiral ligands have amino substituents at the benzylic position. In the arene–chromium complexes, an introduction of the desired func-

tional groups on the side chain can be performed stereoselectively. For further development of the chiral (arene)chromium complexes in the catalytic asymmetric reactions, other functional chelating groups at the benzylic position are required. Here we wish to describe the facile preparation of novel enantiomerically pure chelating arylphosphine ligands which have the planar chirality and functional groups on the side chain, and their use for the catalytic asymmetric alkylation of 1,3-diphenyl-1-acetoxypropene.

2. Results and discussion

2.1. Synthesis and structure of (arene)chromium complexes as chiral ligands

(η^6-Arene)chromium complexes have some significant properties owing to the strong electron-withdrawing ability and steric bulkiness of the coordinated transition metal, and their applications to organic synthesis have been developed. Chromium-complexed arene hydrogen atoms are easily lithiated to functionalize at an appropriate position [4]. Also, the benzylic position of the (arene)chromium complexes is stabilized as the carbocations and are reacted with some nucleophiles via the S_N1 reaction to form the substitution products. This

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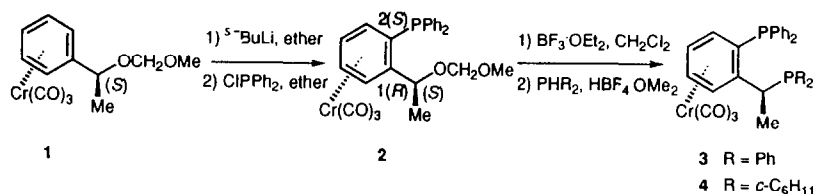
Scheme 1.

S_N1 reactions proceed stereoselectively with retention of the benzylic configuration [5], but no substitution reactions with diorganophosphine reagents, to our knowledge, have been reported in the literature. We have initially studied the preparation of the (arene)chromium complexes having diphosphino groups at the benzylic position and on the aromatic part utilizing the characteristic properties of the (arene)chromium complexes. (S)-Tricarbonyl(1-phenylethyl methoxymethylether)chromium (1) was diastereoselectively lithiated with ^{s}BuLi in ether according to the literature method [6] followed by trapping with chlorodiphenylphosphine gave (1R, 2S),α(S)-phosphine complex 2 with a 50% yield without isolation of any regioisomeric compounds (Scheme 1). For the introduction of the phosphino group at the benzylic position of 2, deprotection of an MOM group was carried out with boron trifluoride etherate in methylene chloride to afford the corresponding benzylalcohol complex, albeit with a 38% yield. Reaction of the resulting benzylalcohol chromium complex with diphenylphosphine or dicyclohexylphosphine in the presence of tetrafluoroboric acid dimethyletherate produced the corresponding chiral diphosphino complexes 3 and 4 as yellow crystals without formation of the corresponding stereoisomeric isomers. The chiral ligand 3 with two diphenylphosphino groups was obtained with a 80% yield in methylene chloride at room temperature, and the corresponding dicyclohexylphosphine–diphenylphosphine ligand 4 was prepared with a 51% yield by refluxing in chloroform. This nucleophilic substitution at the chromium-complexed benzylic posi-

tion proceeded stereoselectively in the retention and the configuration of 3 was confirmed by X-ray crystallography. In addition, the chiral phosphine ligands with a chelating amino group on the side chain were also prepared. The ligand 6 with two amino group on the side chain was synthesized from (R)-tricarbonyl-[N,N,N'-trimethyl-N'-(α(R)phenylethyl)ethylenediamine]chromium (5) [2b] by diastereoselective ortho lithiation in ether with ^{t}BuLi at −78°C according to the method [2c,6] for the preparation of ligand 8 (Scheme 2). For the investigation of the electronic effect of the ligands in the catalytic asymmetric reactions, one of tricarbonyl group on the chromium complex 6 was replaced with an electron-donating triphenylphosphine under photoirradiation with a high pressure mercury lamp to give the phosphine ligand 7 with a 66% yield.

In order to determine the absolute configuration of the diphosphino ligand 3 and furthermore to understand the coordination behavior of this ligand in the asymmetric reaction, crystal structure determination was carried out (Fig. 1). Given the absolute configuration (1R, 2S),α(S) of the starting material 2, the present crystal structure confirms the expected retention of the configuration at the stereogenic center upon the nucleophilic substitution [5,7]. The diphenylphosphino group directly attached to the arene ring of the ligand 3 is oriented in such a way that the phosphorus lone pair points slightly below the chromium complexed arene plane in the solid state. Relevant torsion angles are C(3)–C(2)–P(2)–C(27) of 57.3(3)° and C(3)–C(2)–P(2)–C(21) of −48.3(3)°. The conformation of the side chain allows
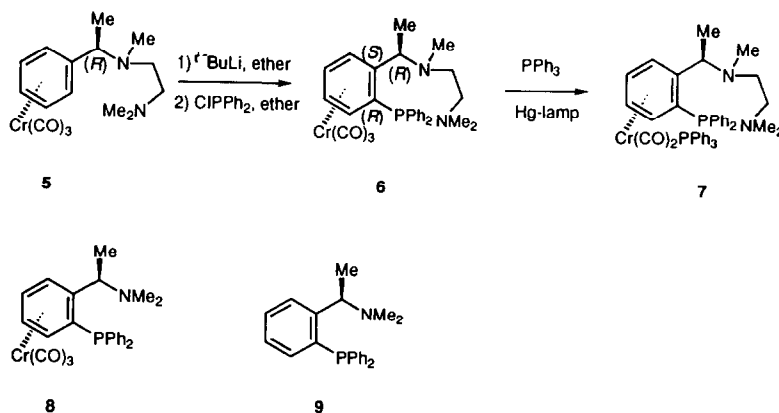
Scheme 2.

the bulky PPh$_2$ group to avoid the steric interactions with the rest of the molecule. The consequence is that the two smaller substituents attached to the stereogenic carbon atom (H and Me) are forced below the functionalized arene ring. This is illustrated by the torsion C(6)–C(1)–C(7)–C(8) angle of 18.7(4)°. Furthermore, the position of the phosphorus atom of the side chain is best reflected by the torsion P(1)–C(7)–C(1)–C(2) angle of 67.1(3)°. This takes one of the phenyl groups in a pseudo axial position and, thus, in closer vicinity to the CO ligand on the chromium. Two phosphorus lone-pair vectors are nearly parallel and approximately face each other in solid state.

2.2. Catalytic asymmetric allylic alkylation of 1,3-diphenyl-1-acetoxypropene

Since we cast the chiral phosphine ligands with additional chelating groups such as amine or phosphine on the side chain containing (η^6-arene)chromium complexes, we turned our attention to the catalytic asymmetric alkylation of 1,3-diphenyl-1-acetoxypropene [8]. Reaction results are summarized in Table 1. Reaction of racemic 1,3-diphenyl-1-acetoxypropene (10) with sodium dimethyl malonate in the presence of 5 mol.% Pd(0) catalyst, generated in situ by mixing [PdCl(η^3-C$_3$H$_5$)]$_2$ with the chiral diphosphine ligand 3, under the standard conditions gave the alkylation product (+)-(R)-11 with a good yield (Scheme 3). The enantioselectivity of the coupling product was largely dependent upon the reaction conditions. Enantioselectivity was increased at a lower reaction temperature (88% ee at −45°C). With the dicyclohexylphosphine ligand 4, the alkylation product (+)-11 was obtained with comparable enantioselectivity. On the contrary, the asymmetric

Fig. 1. Crystallographic structure of 3.

Table 1
Catalytic asymmetric alkylation of 10

Entry	(Arene)-ligand	Solvent	Temperature, (°C)	Time (h)	Yield (%)	% ee of 11 (absolute configuration)
1	3	THF	−25	23	90	61 (R)
2	3	THF	−45	84	88	88 (R)
3	4	THF	−50	19	99	48 (R)
4	4	THF	−78	4.5	48	86 (R)
5	6	THF	−25	43	41	94 (S)
6	7	THF	−25	71	44	76 (S)
7	8	DMF	RT	21	80	68 (S)
8	8	MeCN	RT	46	83	74 (S)
9	8	THF	−25	20	73	92 (S)
10	9	THF	−25	22	50	14 (S)

THF, tetrahydrofuran; DMF, dimethyl formamide; RT, room temperature.
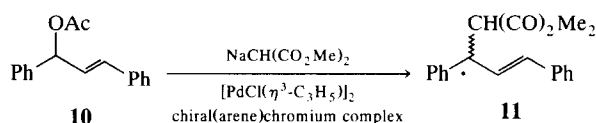
Scheme 3.

reaction catalyzed by the chiral amino phosphine ligand 8 gave an antipode (−)-(S)-alkylated product 11. Employment of the chiral ligand 6 with an additional amino group on the side chain resulted in 94% ee under the same conditions. However, a lower stereoselectivity was observed with diamino diphosphine ligand 7. This lower selectivity would be contributed to an enhancement of the π-electron density of the chromium-complexed arene ring, and thus the π acceptor character of the diphenylphosphino group was diminished. Both amino phosphine ligands 6 and 8 resulted in slightly higher enantioselectivity but showed catalytic activity with lower magnitude than those obtained with the diphosphine ligands. A chiral aminoalkylphosphine ligand, (R)-1-(2-diphenylphosphinophenyl)ethyl-N,N-dimethylamine (9), which is analogous to 8 but lacks the chromium tricarbonyl coordination, resulted in less enantioselectivity (14% ee). The coordination of Cr(CO)$_3$ group to the arene ring as the chiral ligands is essential for the achievement of high stereoselective asymmetric allylic alkylation. For this particular reaction, the combination of diphenylphosphino and amino fragments in the (arene)chromium complexes as the chiral ligand ensures the best control of stereoselectivity so far, because both the steric and the electronic features of this ligand are acting in a cooperative manner. From the results, the chiral (arene)chromium complexes were found to be useful ligands in the asymmetric alkylation of 1,3-diphenyl-1-acetoxypropene as well as ferrocene constitute [3i,j].

Compounds 3, 4, 6 and 8 are representatives of a series of easily accessible chiral chelating ligands in which the two heteroatoms can be introduced independently in consecutive synthetic steps. Such a preparation
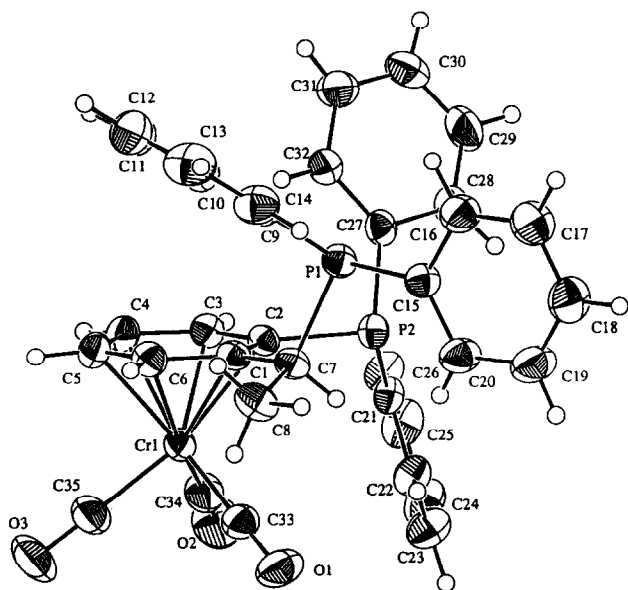
warrants great flexibility, and the approach should allow fine tuning of the ligands, with respect to both their steric and their electronic properties. Work directed towards the extension of the different ligands and further applications in homogeneous asymmetric reactions, including mechanistic studies, is in progress.

3. Experimental details

All manipulations involving organometallics were carried out under an atmosphere of nitrogen or argon and using inert gas–vacuum double-manifold techniques. All melting points were determined on a Yanagimoto MPJ-2 micromelting-point apparatus and are uncorrected. ^{1}H NMR spectra were measured on a Hitachi R-90H or a JEOL GX-400. ^{31}P NMR spectra were determined on a JEOL α-400 and recorded with 85% H_3PO_4 as an external standard. All NMR spectra were recorded in $CDCl_3$ solvent with tetramethylsilane as an internal reference. IR spectra were recorded on a JASCO A-100 spectrometer. Mass spectra were taken on JEOL AX-500 spectrometer. Elemental analysis was performed on a Perkin–Elmer model 240 analyzer. Optical rotations were obtained on a JASCO DIP-370 automatic polarimeter at wavelength 589 nm (sodium D line) using a 1.0 dm cell with a total volume 3 ml.

3.1. (1R,2S),(α,S)-Tricarbonyl[α(o-diphenylphosphino-phenyl)ethyl methoxymethylether] chromium (2)

A solution of ^{s}BuLi (1.3 M in cyclohexane; 1.9 ml, 2.47 mmol) was added to a solution of **1** (0.50 g, 1.65 mmol) in dry ether (20 ml) at −78°C under argon, and the reaction mixture was warmed to −40°C over 1 h. To the reaction mixture was added chlorodiphenylphosphine (0.44 ml, 2.47 mmol), and the mixture was warmed to −10°C and quenched with saturated aqueous NH_4Cl and extracted with ether. The extract was washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel (30 g) chromatography with ether : hexane (1 : 4) to give 0.39 g (50%) of **2**. Melting point (m.p.), 125°C. $[\alpha]_D^{27}$. +208.6° (c 0.62, $CHCl_3$)^{1}H NMR (400 MHz); δ 1.61 (d, J = 6.1 Hz, 1H), 3.09 (s, 3H), 4.13 (d, J = 6.7 Hz, 1H), 4.36 (d, J = 6.7 Hz, 1H), 4.72 (d, J = 6.1 Hz, 1H), 5.18 (t, J = 6.1 Hz, 1H), 5.26 (q, J = 6.1 Hz, 1H), 5.46–5.50 (m, 2H), 7.33–7.40 (m, 10H) ppm. ^{31}P NMR (161.7 MHz): δ − 11.25 (s) ppm. IR ($CHCl_3$); δ 1970, 1900 cm^{-1}. Anal. Found: C, 61.78; H, 4.82. $C_{25}H_{23}O_5PCr$ Calc.: C, 61.72; H, 4.72%.

3.2. Preparation of diphosphine ligands 3 and 4

3.2.1. Preparation of 3

To a mixture of **2** (0.20 g, 0.41 mmol) in dry methylene chloride (20 ml) was added BF_3–OEt_2 (0.06

ml, 0.50 mmol) at 0°C under argon, and the mixture was warmed to room temperature over 1 h. The reaction mixture was quenched at 0°C with water and extracted with methylene chloride. The extract was washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by silica gel (20 g) with ether : hexane (1 : 1) to give 0.066 g (38%) of tricarbonyl(o-diphenylphosphinophenyl ethylalcohol)chromium. M.p., 42°C, $[\alpha]_D^{27}$. + 304° (c 0.19, $CHCl_3$). ^{1}H NMR (400 MHz); δ 1.49 (d, J = 6.1 Hz, 3H), 1.64 (brs, 1H), 4.74 (m, 1H), 5.17 (q, J = 6.1 Hz, 1H), 5.44–5.50 (m, 3H), 7.39–7.41 (m, 10H) ppm, ^{31}P NMR; δ − 12.33 (s) ppm. IR ($CHCl_3$): ν 3400–3200, 1980, 1900 cm^{-1}. To a mixture of the resulting chromium complex (60 mg, 0.14 mmol) and diphenylphosphine (29 mg, 0.16 mmol) in dry CH_2Cl_2 (10 ml) was added $HBF_4 \cdot OMe_2$ (0.020 ml, 0.14 mmol) at 0°C under argon. The reaction mixture was stirred at room temperature for overnight and quenched with water. The mixture was extracted with CH_2Cl_2, and the extract was washed with brine, dried over $MgSO_4$ evaporated in vacuo. The residue was purified by silica gel (20 g) with ether : hexane (1 : 4) to give 66 mg (81%) of **3**. M.p., 196°C. $[\alpha]_D^{30}$: + 317° (c 0.50, $CHCl_3$). ^{1}H NMR (400 MHz): δ 1.27 (dd, J = 5.5, 6.7 Hz, 3H), 4.52 (m, 1H), 4.65 (q, J = 6.7 Hz, 1H), 5.03 (d, J = 6.1 Hz, 1H), 5.12 (t, J = 6.1 Hz, 1H), 5.31 (t, J = 6.1 Hz, 1H), 7.20–7.50 (m, 20H) ppm. ^{31}P NMR (161.7 MHz): δ 10.4 (d, J = 20.5 Hz), − 17.5 (d, J = 20.5 Hz) ppm. IR ($CHCl_3$): ν 1970, 1890 cm^{-1}. Anal. Found: C, 69.12; H, 4.74. $C_{35}H_{28}O_3P_2Cr$ Calc.: C, 68.85; H, 4.63%.

3.2.2. Preparation of 4

The chiral diphosphine ligand **4** was prepared by a similar method to that for **3**. A mixture of tricarbonyl(o-diphenylphosphinophenylethylalcohol)chromium (120 mg, 0.27 mmol), dicyclohexylphosphine (0.07 ml, 0.33 mmol) and $HBF_4 \cdot OMe_2$ (0.05 ml, 0.27 mmol) was refluxed for overnight under argon. A usual work-up gave 86 mg (51%) of **4**. M.p., 193°C, $[\alpha]_D^{27}$: + 31.5° (c 3.25, $CHCl_3$). ^{1}H NMR (400 MHz): δ 0.70–1.35 (m, 11H), 1.40–1.85 (m, 11H), 1.46 (dd, J = 4.3, 7.3 Hz), 3.98 (q, J = 7.3 Hz, 1H), 5.10 (m, 2H), 5.18 (m, 1H), 5.51 (m, 1H), 7.30–7.45 (m, 10H) ppm. ^{31}P NMR (161.7 MHz): δ 19.6 (d, J = 38.1 Hz), − 18.5 (d, J = 38.1 Hz) ppm. IR ($CHCl_3$): ν 1960, 1890 cm^{-1}. Anal. Found: C, 66.78; H, 6.48. $C_{35}H_{40}O_3P_2Cr$ Calc.: C, 66.86; H, 6.62%.

3.3. Preparation of diamino phosphine ligand 6

A solution of **5** (1.0 g, 2.9 mmol) in dry ether (20 ml) was added to ^{t}BuLi in pentane (1.7 M, 2.6 ml, 4.4 mmol) at − 78°C under argon. The mixture was warmed to − 40°C over 1 h and chlorodiphenylphosphine (0.78 ml, 4.4 mmol) was added to the above mixture. The reaction mixture was warmed to − 10°C and quenched

with saturated aqueous NH_4Cl. A usual work-up gave 0.39 g (25%) of **6**. M.p., 123°C. $[\alpha]_D^{28}$: $-346°$ (c 0.57, $CHCl_3$). ^1H NMR (400 MHz): δ 1.16 (d, $J = 6.7$ Hz, 3H), 1.30–1.80 (m, 4H), 1.93 (s, 3H), 2.03 (s, 6H), 4.65 (t, $J = 6.7$ Hz, 1H), 4.99 (d, $J = 6.1$ Hz, 1H), 5.09 (t, $J = 6.1$ Hz, 1H), 5.14 (m, 2H), 7.28–7.33 (m, 10H) ppm. ^{31}P NMR (161.7 MHz): $\delta - 13.76$ (s) ppm. IR $(CHCl_3)$: ν 1980, 1900 cm^{-1}. Anal. Found: C, 63.77; H, 6.06; N, 5.16. $C_{28}H_{35}N_2O_3PCr$ Calc.: C, 63.87; H, 5.93; N, 5.32%.

3.4. Preparation of 7 by photoirradiation

A solution of **6** (200 mg, 0.38 mmol) and PPh_3 (198 mg, 0.75 mmol) in benzene (20 ml) was irradiated with a high pressure mercury lamp for 1 h under nitrogen at room temperature. The precipitate was filtered off, and the filtrate was evaporated in vacuo. The residue was purified by silica gel (10 g) with ether : hexane (1 : 1) to give 175 mg (66%) of **7**. M.p., 84°C. $[\alpha]_D^{28} - 206.3°$ (c 0.13, $CHCl_3$). ^1H NMR (400 MHz): δ 0.89 (d, $J = 6.7$ Hz, 3H), 1.81 (s, 3H), 1.99 (s, 6H), 1.19–1.22 (m, 4H), 3.48 (q, $J = 6.7$ Hz, 1H), 3.45–3.50 (m, 4H), 7.27–7.43 (25H) ppm. ^{31}P NMR (161.7 MHz): δ -12.6 (s), -57.5 (s) ppm. IR $(CHCl_3)$: ν 1970, 1890, 1840 cm^{-1}. Anal. Found: C, 71.26; H, 6.36; N, 3.52. $C_{45}H_{46}N_2O_2P_2Cr$ Calc.: C, 71.03; H, 6.11; N, 3.68%.

3.5. Typical procedure for palladium(0)-catalyzed asymmetric alkylation of 10 in the presence of (arene)-chromium complex

To a mixture of racemic 1,3-diphenyl-1-acetoxypropene **(10)** (200 mg, 0.79 mmol), chiral ligand **8** (37 mg, 0.079 mmol) and $[Pd(\eta^3 - C_3H_5)Cl]_2$ (7.3 mg, 0.020 mmol) in dry THF (2.5 ml) was added a solution of sodium dimethyl malonate (prepared from NaH (60% in oil, 36 mg, 0.95 mmol) and dimethylmalonate (148 mg, 0.95 mmol) in dry THF (2 ml)) at $-25°C$ under argon. The reaction mixture was stirred at the same temperature for 44 h and quenched with aqueous NH_4Cl and extracted with ether. The extract was washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by silica gel chromatography to give alkylated product **11**. The enantioselectivity was determined by high performance liquid chromatography with chiralpack AD (eluted with 5% of 2-propanol in hexane; 1.0 ml min^{-1}; 40°C); retention times, 48 min for the (S) isomer and 73 min for the (R) isomer.

4. Supplementary material available

A crystallographic data, complete list of bond lengths and angles, and tables of thermal parameters and hydro-

gen atom coordinates for **3** have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgments

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