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Synthesis of the Chiral Triphosphine (*S*,*S*)-PhP($CH_2CHMeCH_2PPh_2$)$_2$ and Its Metal Complexes

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The chiral triphosphine ligand (*S*,*S*)-PhP($CH_2CHMeCH_2PPh_2$)$_2$, ttp*, was synthesized by the reaction of (*S*)-$Ph_2PCH_2CHMeCH_2Cl$ and $PhPH_2$ in the presence of LDA. Reactions of ttp* with $RuCl_2(PPh_3)_3$, $[RhCl(COD)]_2$, and $CoCl_2$ produced $RuCl_2$(ttp*), RhCl(ttp*), and $CoCl_2$(ttp*), respectively. These compounds were characterized by elemental analysis and multinuclear NMR spectroscopy. The structure of RhCl(ttp*) has been determined by X-ray diffraction.

Introduction

Polydentate phosphines offer several advantages as ligands in homogeneous catalysis.[1] They may provide more control of metal coordination number and stereochemistry and limit intra- and intermolecular ligand exchange. In the past three decades, a number of polydentate phosphine ligands have been synthesized and their organometallic chemistry intensively investigated.[1,2] A variety of catalytic properties have been observed for these complexes, for example, in the hydrogenation of olefins, selective reductions of α,β-unsaturated ketones to allylic alcohols, and the hydrogenation and oligomerization of acetylenes.

Although on the one hand a large number of reports have been published on polyphosphines and their metal complexes, and on the other hand there have been intensive studies on asymmetric catalysis using chiral monodentate and bidentate phosphines,[3] metal complexes with chiral polydentate phosphines have received little attention. Previous studies on asymmetric catalysis with phosphine ligands have demonstrated that chiral diphosphine ligands are more efficient in inducing asymmetric reactions than chiral monodentate phosphines. The ligand chelation is believed to play an important role in stereochemical control by restricting the number of competing asymmetric conformations surrounding a metal center. Thus a properly designed chiral polydentate phosphine ligand may provide a higher degree of stereochemical control surrounding a metal center and therefore may induce a higher stereoselectivity.

Tridentate phosphine ligands are particularly interesting for applications in asymmetric catalysis. Because many homogeneous catalysts or intermediates are five- or six-coordinated metal complexes, tridentate ligands can provide both rigorous control of the stereochemistry and reactivity of the resulting complexes and still allow sufficient available coordination sites for incoming substrates. To date only a few chiral chelating tridentate phosphine ligands have been synthesized and investigated for asymmetric catalysis. The novel chiral tripod ligands tris(phospholane),[4] (*S*,*S*,*S*)-MeSi($CH_2P(t$-$Bu)Ph)_3$,[5] and $CH_3C(CH_2PR_2)(CH_2PR'_2)(CH_2PR''_2)$[6] were reported recently. Chiral linear tridentate phosphine ligands in which the phosphorus donor atoms are linked by two methylene groups are also known, for example, $PhP(CH_2CH_2PPhAn)_2$ (An = *p*-$CH_3OC_6H_4$),[7] $PhP(CH_2CH_2PPh(Nmen)_2$ (Nmen = neomenthyl),[8] and a bis(phospholane) ligand.[4a] Other examples of chiral tridentate phosphines include $PhAnPCH(CH_2CH_2PPhAn)_2$[7] and 1,3-($PPh_2C^*HR)_2C_6H_4$.[9]

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The triphosphine ligands of type $PhP(CH_2CH_2CH_2PR_2)_2$ are one of the most often used tridentate phosphine ligands in recent studies on organometallic chemistry.[10] Catalytic properties have been observed for their metal complexes, for example, the complex [RhH(ttp)] (ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$) was reported to be a very active catalyst for the hydrogenation of alkenes.[11] We are interested in preparing a series of chiral linear triphosphine ligands structurally analogous to $PhP(CH_2CH_2CH_2PR_2)_2$ with chiral centers at different positions of the backbone or on the terminal phosphorus atoms and investigating the potential uses of these chiral ligands in asymmetric catalysis. In this report, the synthesis of the chiral triphosphine ligand (*S*,*S*)-$PhP(CH_2CHMeCH_2PPh_2)_2$, ttp*, and its metal complexes is described.

Experimental Section

All reactions were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under dinitrogen over sodium benzophenone (hexane, diethyl ether, THF), sodium (toluene), or calcium hydride (dichloromethane). Microanalyses were performed by MEDAC Ltd (Middlesex, U.K.) or MHW Lab (Phoenix, AZ). Mass spectra were obtained in a Finnigan TSQ 7000 spectrometer. ^1H, ^{31}P, and ^{13}C NMR spectra were collected on JEOL EX-400 or Bruker ARX-300 spectrometers. ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. $[Rh(COD)Cl]_2$,[12] $RuCl_2(PPh_3)_3$,[13] and $RuCl_2(DMSO)_4$[14] were prepared according to literature methods. All other reagents were used as purchased from Aldrich Chemical Co.

(*S*)-3-(Diphenylphosphinyl)-2-methyl-1-propanol, 1. A 20 g amount of (*S*)-(+)-3-bromo-2-methyl-1-propanol (13.07 mmol) dissolved in 10 mL of THF was added dropwise to a mixture of 28.75 mL of 0.5 M potassium phosphide (14.38 mmol) and 95.87 mL of 1.5 M LDA (14.38 mmol) in THF. During addition, the reaction mixture was cooled in an ice bath and after was stirred for 0.5 h. The ^{31}P NMR spectrum of the reaction mixture (after hydrolysis) showed a singlet at δ −22.1 ppm which was assigned to (*S*)-$Ph_2PCH_2CHMeCH_2OH$. The solvent was then removed completely by vacuum. Water (200 mL) and benzene (300 mL) were added. The benzene layer was separated, and 30 mL of H_2O_2 was added to speed up the oxidation. The mixture was stirred in air overnight. More water was added, and the benzene layer was separated. The solvent was removed to give a colorless oil. Yield: 34.1 g, 95%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.00 (dd, *J* = 6.84, 1.47 Hz, 3H, CH_3), 2.09−2.13 (m, br, 1H, CH_3C*H*), 2.34−2.37 (m, 2H, $O{=}PCH_2$), 3.47 (dd, *J* = 11.2, 7.8 Hz, 1H, C*H*OH), 3.62 (dd, *J* = 11.7, 3.4 Hz, 1H, C*H*OH), 7.44−7.80, (m, 10H, $O{=}PPh_2$). $^{31}P\{^1H\}$ NMR (161.84 MHz, $CDCl_3$): δ 33.5 (s).

(*S*)-3-(Diphenylphosphinyl)-2-methyl-1-chloropropane, 2. A mixture of 34.1 g of **1** (130.7 mmol), 26.16 g of tosyl chloride (137.2 mmol), 19 mL of pyridine (261.4 mmol), and 45 g of benzyltriethylammonium chloride (196.1 mmol) in 100 mL of chloroform was refluxed overnight. Ether (200 mL) and water (50 mL) were added, and the organic layer was washed successively with 2 M HCl, 5% $NaHCO_3$, and water and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was column chromatographed (10% ether/hexane) to yield a white solid. Yield: 21.9 g, 60%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.14 (d, *J* = 6.84 Hz, 3H, CH_3), 2.11−2.20 (m, 1H, O=PCH), 2.38−2.43 (m, 1H, CH_3C*H*), 2.57−2.64 (m, 1H, O=PCH), 3.49−3.56 (m, 2H, CH_2Cl), 7.44−7.81 (m, 10H, $O{=}PPh_2$). $^{31}P\{^1H\}$ NMR (161.84 MHz, $CDCl_3$): δ 29.4 (s).

(*S*)-3-(Diphenylphosphino)-2-methyl-chloropropane, 3. A benzene solution (200 mL) of 21.9 g of **2** (74.7 mmol), 40 mL of trichlorosilane (396.3 mmol), and 50 mL of triethylamine was stirred at room temperature for 3 h. The mixture was diluted with benzene, and 30% aqueous sodium hydroxide was added cautiously until all the solid dissolved. The benzene layer was then separated, washed with water, and dried by passing through a column of $MgSO_4$. The solvent was then pumped away. The product was dried under vacuum overnight. Yield: 18.6 g, 90%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.16 (d, *J* = 6.4 Hz, 3H, CH_3), 1.90−1.98 (m, 2H, PCH_2), 2.30−2.33 (m, 1H, CH_3C*H*), 3.57 (d, *J* = 4.9 Hz, 2H, C*H*$_2$OH), 7.31−7.47 (m, 10H, PPh_2). $^{31}P\{^1H\}$ NMR (161.84 MHz, $CDCl_3$): δ −22.3 (s).

(*S*,*S*)-$PhP(CH_2CHMeCH_2PPh_2)_2$, ttp*, 4. To a mixture of 17.89 g of **3** (64 mmol) and 3.56 mL of phenylphosphine (32.4 mmol) in 150 mL of THF was added dropwise 46 mL of 1.5 M lithium diisopropylamide (64 mmol) in THF. After addition, the solution was stirred overnight at room temperature. The solvent was then pumped away by vacuum, and water (150 mL) was added followed by benzene (200 mL). The benzene layer was separated and dried by passing through a column of $MgSO_4$. The solvent was then completely removed by vacuum to give a light yellow oil. The product was dried under vacuum overnight. Yield: 18.8 g, 98.6%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.19 (d, *J* = 6.4 Hz, 3H, CH_3), 1.14 (d, *J* = 5.86 Hz, 3H, CH_3), 1.45−2.51 (m, 10H, $2CH_2CHCH_2$), 6.95−7.48 (m, 20H, $2PPh_2$). $^{31}P\{^1H\}$ NMR (161.84 MHz, C_6D_6): δ −37.8 (s), −22.8 (s), −22.0 (s). $[\alpha]^{25}_D$ = 17.95° ($CHCl_3$). MS/CI: *m*/*z* (relative intensity) = 591 (80) ($M + H^+$), 349 (100) ($M - CH_2CHMeCH_2PPh_2{}^+$).

1-(Diphenylphosphinyl)-2-methylcyclopropane, 5. To a 50 mL THF solution of 7.15 g (24.43 mmol) of **3** was added dropwise 17.9 mL of 1.5 M lithium diisopropylamide solution in THF (26.87 mmol). During addition, the reaction mixture was cooled in an ice bath. After addition, the solution was stirred at room temperature for 6 h. The solvent was removed by reduced pressure, and water (100 mL) was added followed by benzene (120 mL). The benzene layer was separated and dried by anhydrous $MgSO_4$. The solvent was then removed by reduced pressure. The crude product was purified by passing through a silica gel column using ethyl acetate/methanol as eluent. A white solid was obtained after the solvent was removed by reduced pressure and vacuum. Yield: 4.69 g, 75.0%. Mp: 135−137 °C. $[\alpha]^{25}_D$ = +19.75° ($CHCl_3$). Anal. Calcd for $C_{16}H_{17}PO$: C, 74.80; H, 6.79. Found: C, 74.99; H, 6.69. ^1H NMR (300 MHz, acetone-d_6): δ 0.68−0.74 (m, 1H, CH), 1.04−1.13 (m, 1H, CH), 1.18 (d, *J* = 4.9 Hz, 3H, CH_3), 1.30−1.40 (m, 2H, CH_3C*H*, C*H*P), 7.49−7.54, 7.77−7.80 (m, 10H, Ph). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6): δ 27.1 (s). $^{13}C\{^1H\}$ NMR (75.47 MHz, acetone-d_6): δ 10.68 (d, ^2J(P−C) = 4.6 Hz, CH_2), 11.44 (d, ^2J(P−C) = 3.3 Hz, CH_3CH), 15.39 (d, ^1J(P−C) = 103.9 Hz, PCH), 17.87 (d, ^3J(P−C) = 2.9 Hz, CH_3), 128.71 (d, *J*(P−C) = 4.1 Hz, Ph), 128.86 (d, *J*(P−C) = 4.0 Hz, Ph), 131.06 (s, Ph), 131.18 (s, Ph), 131.66 (t,

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2.5, Ph), 136.0 (d, ^1J(P-C) = 15.3 Hz, O=PC), 137.4 (d, ^1J(P−C) = 15.9 Hz, O=PC).

RhCl(ttp*), 6. To a boiling slurry of 0.09 g of [Rh(COD)-Cl]$_2$ (COD = 1,5-cyclooctadiene) (0.184 mmol) in 40 mL of ethanol was added 10 mL of a benzene solution of 0.29 g (0.491 mmol) of ligand ttp*. After addition of the benzene solution of the ligand, all of the [Rh(COD)Cl]$_2$ dissolved quickly and the solution changed to a deep orange color. The volume of the solution was reduced by vacuum, and a yellow solid began separating from the solution. The solid was collected on a filter frit, washed with small amount of ethanol and diethyl ether, and dried under vacuum. Yield: 125 mg (93%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.73 (d, J = 4.6 Hz, CH$_3$), 0.84 (d, J = 5.7 Hz, CH$_3$), 1.20−2.50 (m, 10H, 2CH$_2$CHCH$_2$), 6.80−8.50 (m, 20H, 2PPh$_2$). ^{31}P{^{1}H} NMR (161.70 MHz, C$_6$D$_6$, AMM′X (X = Rh) system): δ 13.9 (M, PPh$_2$), 14.8 (M′, PPh$_2$), 28.0 (A, PPh); J(Rh−PPh) = 166.5 Hz, J(Rh−PPh$_2$) = 126 Hz, J(PPh−PPh$_2$) = 49.9 and 55 Hz, J(PPh$_2$−PPh$_2$) = 274.8 Hz. These coupling constants were obtained by simulation. Anal. Calcd for C$_{38}$H$_{41}$ClP$_3$Rh: C, 62.61; H, 5.67. Found: C, 62.78; H, 5.81.

RuCl$_2$(ttp*), 7. A mixture of 0.37 g of ttp* (0.627 mmol) and 0.51 g of RuCl$_2$(PPh$_3$)$_3$ (0.533 mmol) in ca. 40 mL of acetone was stirred overnight at room temperature to give a reddish orange solution. The solvent was then removed completely and ether was added to give a reddish orange precipitate. The solid was collected on a filter frit and dried under vacuum overnight. Yield: 0.38 g (41%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.04−0.14 (m, 1H, 2CH$_2$CHCH$_2$), 0.59−0.64 (m, 3H, CH$_3$), 0.99 (t, J = 3.0 Hz, 3H, CH$_3$), 1.34−1.43 (m, 2H, 2CH$_2$CHCH$_2$), 1.66−1.76 (m, 2H, 2CH$_2$CHCH$_2$), 2.05−2.26 (m, 3H, 2CH$_2$CHCH$_2$), 3.36−3.64 (m, 2H, 2CH$_2$CHCH$_2$), 6.76−8.56 (m, 25H, aromatic protons). ^{31}P{^{1}H} NMR (121.49 MHz, C$_6$D$_6$): δ 33.5 (dd, J = 41.3, 26.6 Hz), 55.0 (dd, J = 71.6, 26.6 Hz), 61.7 (dd, J = 71.6, 41.3 Hz). Anal. Calcd for C$_{38}$H$_{41}$Cl$_2$P$_3$-Ru: C, 59.85; H, 5.42. Found: C, 59.85; H, 5.47.

CoCl$_2$(ttp*), 8. To a solution of 0.22 g of ttp* (0.373 mmol) in 20 mL of methanol was added 34 mg of CoCl$_2$ (0.261 mmol). Immediately after addition, a red solid began to separate. The solid was collected on a filter frit, washed with small amount of diethyl ether, and dried in vacuo. Yield: 166 mg (88%). The compound is paramagnetic so no NMR data could be obtained. Anal. Calcd for C$_{38}$H$_{41}$Cl$_2$P$_3$Co: C, 63.34; H, 5.73. Found: C, 63.11; H, 5.57.

Crystallographic Analysis of RhCl(ttp*)·EtOH. Suitable crystals for X-ray diffraction study were obtained by standing a saturated ethanol solution of RhCl(ttp*) at room temperature. A specimen of dimension 0.45 × 0.3 × 0.15 mm was mounted on a glass fiber and used for X-ray structure determination. The crystal system was orthorhombic, and the space group $P2_12_12_1$, consistent with an enantiomerically pure compound, was identified from the systematic absences h00, 0k0, 00l, $2n + 1$ = absent. A total of 7965 intensity measurements were made using the $\omega{-}2\Theta$ scan technique in the range $3 \le 2\Theta \le 65°$ (Mo Kα radiation). Of these 7666 were unique (R_{merge} = 2.06%) and 6739 observed $F \ge 4\sigma(F)$, which were used for structure solution and refinement using the SHELXTL PLUS[15] program package. Solution by direct methods yielded the positions of all non-hydrogen atoms. Refinement by full-matrix least squares resulted in final discrepancy indices R = 0.033 and R_w = 0.035 with GOF = 1.09. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens were revealed in difference Fourier maps but then placed in geometrically determined positions $d_{\text{C−H}}$ = 0.96 Å and refined isotropically with riding constraints and group thermal parameters. The absolute configuration of the structure was confirmed with Roger's test. The data:parameter ratio was 16.2:1, and residual electron density was +0.8/−1.0 e Å^{-3}, due to uncorrected absorption. Further crystallographic details for RhCl(ttp*)·EtOH are given in Table 1. Selected bond distances and angles for RhCl(ttp*)·EtOH are given in Table 2.

Table 1. Crystal Data and Refinement Details for RhCl(ttp*)·EtOH

formula	C$_{40}$H$_{47}$ClOP$_3$Rh
fw	775.0
color and habit	dark red slab
crys dimens (mm)	0.45 × 0.3 × 0.15
crys sys	orthorhombic
space group	$P2_12_12_1$
a, Å	9.734(2)
b, Å	17.751(3)
c, Å	21.337(3)
V, Å^3	3686.7(11)
Z	4
d_{calc}, g cm^{-3}	1.396
abs coeff mm^{-1}	0.697
F(000)	1608
radiation	Mo Kα (λ = 0.071 073 Å)
2θ range, deg	3.0−65
scan type	2θ-θ
scan speed, deg/min	variable; 2.00−60.00 in ω
scan range (w)	0.80° plus Kα separation
T, K	198
std reflcns	3 measd every 150 reflcns
index range	$0 \le h \le 14$, $-1 \le k \le 24$, $-1 \le l \le 30$
reflctn collcda	7965
indepdt reflctns	7666 (R_{int} = 2.06%)
obsd reflcns	6739 ($F > 4.0\sigma(F)$)
abs corr	N/A
system used	Siemens SHELXTL IRIS
quantity minimized	$\Sigma(w(F_o - F_c)^2$
absolute struct	η = 1.12 (5)
extinction corr	χ = 0.00014(4), where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
H atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.003F^2$
no. of params refined	417
final R indices (obsd data)	R = 3.32%, wR = 3.53%
R indices (all data)	R = 4.08%, wR = 3.72%
goodness of fit	1.09
largest and mean Δ/σ	0.02, 0.000
data to param ratio	16.2:1
largest diff peak, e Å^{-3}	0.80
largest diff hole, e Å^{-3}	-1.03

Results and Discussion

Synthesis of the Chiral Ligand. The ligand ttp* was prepared according to Scheme 1. Reaction of Ph$_2$-PK with commercially available (S)-(+)-BrCH$_2$CHMeCH$_2$-OH in THF in the presence of LDA produced quantitatively the monophosphine (S)-Ph$_2$PCH$_2$CHMeCH$_2$OH as indicated by an in situ ^{31}P NMR. The function of LDA here is to remove the hydroxyl proton of (S)-(+)-BrCH$_2$-CHMeCH$_2$OH so that Ph$_2$PK would not be protonated by the OH functional group. The hydroxyl group of (S)-(+)-BrCH$_2$CHMeCH$_2$OH could also be protected using dihydropyran.[16] The monophosphine (S)-Ph$_2$PCH$_2$-CHMeCH$_2$OH was not isolated but was oxidized by H$_2$O$_2$ to give the phosphine oxide (S)-Ph$_2$P(O)CH$_2$-CHMeCH$_2$OH, **1**. Treatment of the phosphine oxide **1** with tosyl chloride always led to a mixture of (S)-Ph$_2$P(O)CH$_2$CHMeCHCH$_2$OTs and (S)-Ph$_2$P(O)CH$_2$-CHMeCHCH$_2$Cl, **2**. Pure compound (S)-Ph$_2$P(O)CH$_2$-CHMeCHCH$_2$Cl, **2**, could be easily obtained by refluxing a mixture of the phosphine oxide **1**, TsCl, and Et$_3$NCH$_2$-PhCl in CHCl$_3$ for 10 h. Reduction of **2** with HSiCl$_3$

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[15] Sheldrick, G. M. SHELXTL PLUS, Siemens Analytical Instruments, 1993.

[16] Greene, T. W.; Wuts, P. G. *Protective groups in Organic Synthesis*, 2nd ed.; John Wiley and Sons: New York, 1991; p 31.

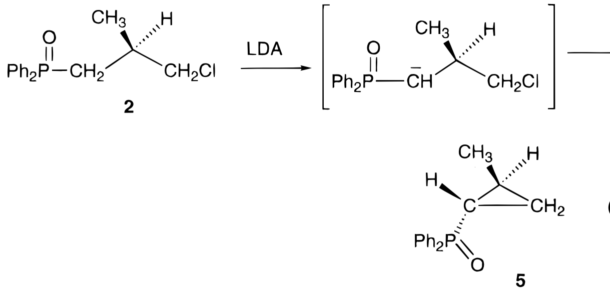
Table 2. Selected Bond Distances (Å) and Angles (deg) for RhCl(ttp*) and Related Compounds

	RhCl(ttp*)	RhCl(ttp)[20]	RhCl(etp)[21]	RhCl(etp*)[4a]
		Interatomic Distances		
Rh(1)−Cl(1)	2.406(1)	2.381(2)	2.4212(9)	2.4018(8)
Rh(1)−P(1)	2.264(1)	2.288(1)	2.2808(1)	2.2658(9)
Rh(1)−P(2)	2.183(1)	2.201(2)	2.1646(8)	2.1453(8)
Rh(1)−P(3)	2.292(1)	2.288(1)	2.2770(8)	2.2730(9)
		Intermolecular Angles (deg)		
Cl(1)−Rh(1)−P(1)	89.3(1)	89.2	95.84(3)	95.60(3)
Cl(1)−Rh(1)−P(2)	178.3(1)	178.8	174.65(3)	178.3(2)
Cl(1)−Rh(1)−P(3)	90.9(1)	89.2	98.78(3)	95.05(3)
P(1)−Rh(1)−P(2)	91.7(1)	90.7	83.08(3)	84.81(3)
P(1)−Rh(1)−P(3)	168.8(1)	171.1	156.19(3)	162.83(3)
P(2)−Rh(1)−P(3)	88.4(1)	90.7	83.98(3)	84.16(3)

produced the key phosphine intermediate (*S*)-$Ph_2PCH_2CHMeCHCH_2Cl$, **3**. A one-pot reaction of **3** with 0.5 equiv of $PhPH_2$ in the presence of LDA produced the desired chiral ligand ttp*, **4**. In the last step of the reaction, LDA was used to generate phosphide species in situ. Similar strategy was used previously in the preparation of polyphosphine ligands[17] and macrocycles.[18]

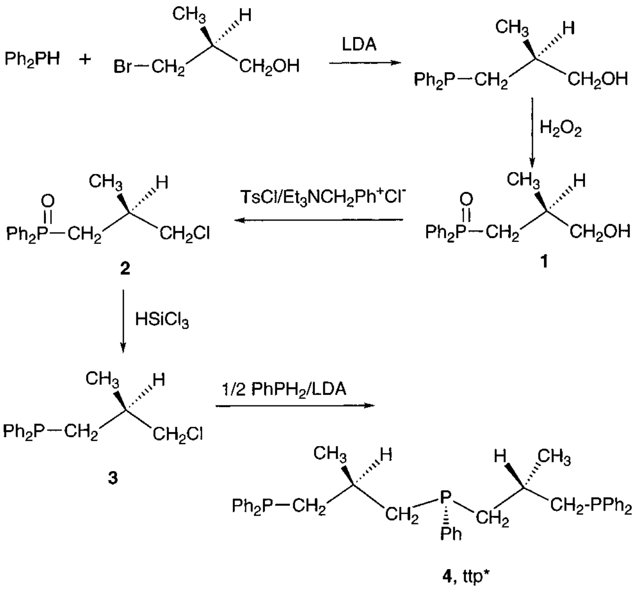
The ligand was characterized by ^1H, ^{31}P, and ^{13}C NMR spectroscopy. In the $^{31}P\{^1H\}$ NMR spectrum, a singlet at −37.8 ppm was observed for the central PhP group, and two singlets at −22.0 and −22.8 ppm were observed for the two chiratropic terminal Ph_2P groups.

It may be noted that alternative routes were also attempted in the course of the ligand synthesis. In an attempt to prepare $PhP(CH_2CHMeCH_2P(O)Ph_2)_2$ from the phosphine oxide **2**, the reaction of the phosphine oxide **2** with 0.5 equiv of $PhPH_2$ in the presence of LDA was carried out. However, the predominant product of this reaction was found to be the cyclic phosphine oxide **5** (eq 1). Thus the proton of the CH_2 group α to the $Ph_2P(O)$ group in compound **2** is deprotonated preferentially to the $PhPH_2$ and an intramolecular reaction occurs. Our attempts to prepare the intermediates $PhP(O)(CH_2CHMeCH_2X)_2$ (X = Cl, OTs) from $PhP(O)(CH_2CHMeCH_2OH)_2$ were also unsuccessful as the latter compound reacts very slowly with $SOCl_2$ or TsCl.

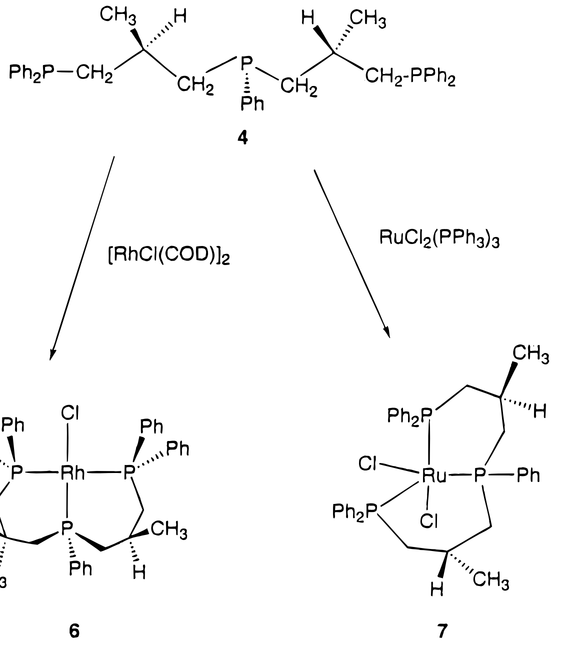


(1)

Scheme 1. Preparation of the Chiral Tridentate Phosphine Ligand



Scheme 2



Synthesis of Metal Complexes. Reaction of ttp* with $[RhCl(COD)]_2$ in a mixed solvent of methanol/benzene produced the orange compound RhCl(ttp*), **6**, in ca. 93% yield (Scheme 2). Similar reactions have been used to prepare the analogous nonchiral complexes RhCl(ttp)[19] and RhCl(etp) (etp = $PhP(CH_2CH_2PPh_2)_2$).[20] The ^{31}P NMR spectra of RhCl(ttp) and RhCl(etp) show simple first-order AM_2X splitting pattern with a doublet of triplets for the unique PPh group and a doublet of doublets for the magnetically equivalent terminal PPh_2 groups. However the $^{31}P\{^1H\}$ NMR spectrum of RhCl(ttp*) in C_6D_6 give an AMM′X pattern. The signals for the terminal PPh_2 group were observed at 13.9 and 14.8

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(19) Nappier, T. E.; Meek, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 306.

(20) Westcott, S. A.; Stringer, G.; Anderson, S. Taylor, N. J.; Marder, T. B. *Inorg. Chem.* **1994**, *33*, 4589.

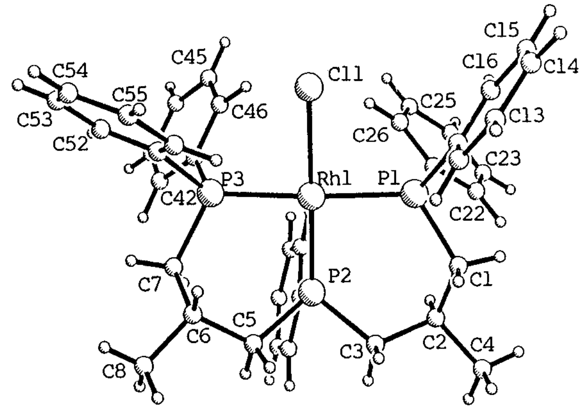

Figure 1. X-ray structure of RhCl(ttp*).

ppm, and the signal for the central P atom was observed at 28.0 ppm. Two signals were observed for the PPh$_2$ groups since they are chiratropic and magnetically inequivalent. In the ^{1}H NMR spectrum, two different signals were also observed for the CH$_3$ groups attached to the backbone of the triphosphine. The spectroscopic data for this compound are consistent with a structure in which the triphosphine is coordinated in a meridional fashion. The structure of RhCl(ttp*) was unambiguously determined by an X-ray diffraction analysis.

The molecular structure of RhCl(ttp*) is shown in Figure 1. The overall geometry around rhodium is square planar. The Rh−Cl and Rh−P bond distances are within the range observed for similar complexes RhCl(ttp)[21] and RhCl(etp).[20] The coordination sphere is similar to that reported for RhCl(ttp) except that the bond distances between rhodium and two terminal phosphorus differ significantly by 0.028 Å in the chiral complex RhCl(ttp*) but are the same by symmetry in RhCl(ttp) and that the angles between P(1)−Rh−P(2) and P(3)−Rh−P(2) are different by 3.3° in the chiral complex RhCl(ttp*) but are identical in RhCl(ttp). It is noted that slightly different bond distances between rhodium and two terminal phosphorus atoms were observed in RhCl(etp) (0.0128 Å) and RhCl(etp*) (0.0072 Å), but angles between P(1)−Rh−P(2) and P(3)−Rh−P(2) are quite similar in these complexes (difference is less than 0.9°). The asymmetric environment around rhodium is clearly seen.

Reactions of ttp* with RuCl$_2$(PPh$_3$)$_3$ or RuCl$_2$(DMSO)$_4$ produced the orange compound RuCl$_2$(ttp*). The ^{31}P NMR spectrum in C$_6$D$_6$ shows three different ^{31}P NMR signals at 33.5 ppm (dd, J = 41.3, 26.6 Hz), 55.0 ppm (dd, J = 71.6, 26.6 Hz), and 61.7 ppm (dd, J = 71.6, 41.3). These chemical shifts and coupling constants are very similar to those reported for *fac*-RuCl$_2$(Cyttp), which has been characterized by X-ray diffraction.[22] The ^{1}H NMR spectra in CDCl$_3$ displays two signals for the methyl protons attached to the backbone. On the basis of the spectroscopic data, the structure of this compound is formulated as the five-coordinated facial compound. It is noted that the structure of analogous nonchiral complex RuCl$_2$(ttp) has been recently confirmed to have a TBP structure with the ttp ligands in a facial geometry.[9] Thus, introducing two methyl group does not change the geometry around ruthenium.

Summary. The chiral triphosphine ligand (S,S)-PhP(CH$_2$C*HMeCH$_2$PPh$_2$)$_2$, ttp*, was synthesized by the reaction of (S)-Ph$_2$PCH$_2$CHMeCH$_2$Cl and PhPH$_2$ in the presence of LDA. Metal complexes of the chiral ligand can be easily prepared.

Acknowledgment. The authors acknowledge the financial support from the Croucher Foundation.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, complete bond lengths and bond angles, anisotropic displacement coefficients, and H atom coordinates and isotropic displacement coefficients for RhCl(ttp*)·EtOH (5 pages). Ordering information is given on any current masthead page.

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