Metal complexes of new chiral tridentate ligands with N, P and S donors: The crystal structure of $[(S)\text{-}Ph_2POCH_2CH(NMe_2)CH_2CH_2SCH_3]W(CO)_3$

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Abstract

Two new ligands, $(S)\text{-}Ph_2POCH_2CH(NMe_2)CH_2CH_2SCH_3$, derived from *L*-methionine, and $(R)\text{-}Ph_2POCH_2CH(NMe_2)CH_2SCH_3$ from L-cysteine have been prepared and characterized. Several metal complexes of Pd, Mo and W have been prepared. These ligands produce a chiral electronically asymmetric environment at the metal that is evidenced by *trans* influences on the other ligands. A crystal structure has been determined for $[(S)\text{-}Ph_2POCH_2CH(NMe_2)CH_2CH_2SCH_3]W(CO)_3$. The sulfur adopts an S_s configuration in the solid and significant *trans* influences are observed in the metrical parameters of the carbonyls. This tungsten complex crystallizes in the monoclinic space group $P2_1$ with $a = 8.8435(6)$ Å, $b = 14.384(1)$ Å, $c = 9.546(1)$ Å, $\beta = 107.051(8)$, $Z = 2$ and $V = 1161.0(4)$ Å^3.

Key words: Tungsten; Molybdenum; Palladium; Chirality; X-ray diffraction; Carbonyl

1. Introduction

Electronic effects play an important role in asymmetric synthesis. We have previously reported that chiral allylmolybdenum complexes having a very asymmetric electronic environment at the metal can be used as reagents in asymmetric synthesis with more than 98% enantiomeric excess in some cases [1]. There is a paucity of information on the role that electronic effects have upon the stereochemical outcome in asymmetric catalysis, especially with regard to non-racemic chiral tridentate ligands [2]. The design of chiral ligands has generally centered on steric bulk to provide the chiral recognition of metal centers. We believe that there is substantial potential in the development of ligands which control reactivity by producing an asymmetric electronic environment at the metal. In this context, a chiral tridentate ligand with three very different donor atoms would appear to be an ideal choice. The NPS donor set in potentially η^3 ligands, such as $Ph_2PCH_2CH(NMe_2)CH_2CH_2SCH_3$, developed by Griffin and Kellogg [3] was attractive. That work has focused on η^2 complexes, and the Pd complexes with these ligands [4] were used as catalysts in asymmetric cross-coupling Grignard reactions, with results that could best be explained by electronic factors. We, on the contrary, were interested in preparing η^3 complexes in order to create a very asymmetric electronic environment in six- and seven-coordinated intermediates, particularly those which might be used with ruthenium, molybdenum and tungsten catalysts. We wish to report the preparation of two new chiral tridentate ligands containing N, P, S donor sets and some representative η^3 and η^2 metal complexes prepared from them.

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2. Experimental details

2.1. General comments

All starting materials were purchased from either Aldrich or Strem. The procedures used to prepare the methylated amino acids and their reduction to methylated amino alcohols were modified from those given in the literature [3–5] and are given below. All nuclear magnetic resonance (NMR) spectra were recorded using a Bruker WM-250, GE Omega 300 or GE QE-300 instrument. IR spectra were recorded on a Nicolet 5SX FTIR instrument. Mass spectra were recorded on a Kratos MS80RFA spectrometer. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA.

2.2. Preparation of (S)-N,N-dimethylmethionine, (S)-$HOOCCH(NMe_2)CH_2CH_2SCH_3$

In a 500 ml round-bottomed flask equipped with a stir bar, *L*-methionine (5.00 g, 33.5 mmol), Pd on activated carbon (5.00 g of 10% Pd), formaldehyde (60 ml, 80.5 mmol; 37% formaldehyde in water), and 200 ml of water were added. The mixture was purged of air by vigorously bubbling nitrogen through it for 10 min. Then H_2 was bubbled through the mixture for 15 min and the mixture was stirred under an atmosphere of H_2 for an additional 12 h. The mixture was heated to boiling in the air and the boiling was continued for 10 min to remove the remaining formaldehyde. The hot reaction mixture was filtered and the remaining Pd catalyst was washed twice with hot water to extract any remaining product. The volatiles were removed from the colorless filtrate with a rotary evaporator to yield a white solid which was recrystallized from ethanol–hexane (yield, 4.74 g, 26.8 mmol (79%)) or could be used directly in the next step. The unrecrystallized product contains a small percentage of water, but it does not interfere with subsequent reduction step. ^{1}H NMR (D_2O, 25°C, 250 MHz): 3.58 (dd, 1H, C*H*COOH); 2.80 (s, 6H, NMe_2); 2.50 (m, 2H, CH_2SCH_3); 2.06 (m, 2H, $CH_2CH_2SCH_3$); 2.03 (s, 3H, SCH_3) ppm.

2.3. Preparation of N,N-dimethyl-S-methylcysteine, (R)-$HOOCCH(NMe_2)CH_2SMe$

The above procedure was repeated with *S*-methyl-L-cysteine (4.53 g, 33.5 mmol), Pd on activated carbon (5.00 g of 10% Pd) and formaldehyde (60 ml, 80.5 mmol (37%)) in 200 ml of water. The product was recrystallized from ethanol–hexane (yield, 3.36 g, 17.4 mmol (52%)). ^{1}H NMR (D_2O, 25°C, 250 MHz): 3.77 (m, 1H, C*H*COOH); 3.06 (m, 2H, CH_2); 2.77 (s, 6H, NMe_2); 2.11 (s, 3H, SCH_3) ppm.

2.4. Preparation of (S)-2-(amino-4-methylthio)-1-butanol, (S)-$HOCH_2CH(NH_2)CH_2CH_2SCH_3$

To a stirred suspension of $LiAlH_4$ (9.5 g, 250 mmol) in 300 ml of dry tetrahydrofuran (THF) chilled in an ice bath was added *L*-methionine (15.0 g, 100 mmol) in small portions over a period of 5 min. After 14 min at 0°C, the solution was allowed to warm to room temperature, stirred for an additional 30 min, subsequently placed under nitrogen and heated under reflux for 4 h. The solution was then cooled to 0°C and hydrolyzed with 10 ml of H_2O, 10 ml of 15% NaOH and 30 ml of H_2O. The solution was filtered and concentrated, yielding a yellow liquid which was taken up in 40 ml of CH_2Cl_2 and washed with brine (1 × 10 ml), dried (Na_2SO_4) and concentrated, yielding 11 g (79%) of a pale-yellow oil. ^{1}H NMR ($CDCl_3$); 3.57 (dd, 1H, J = 10.7 and 3.9 Hz, C*H*HOH); 3.32 (dd, 1H, J = 10.7 Hz and 7.4 Hz, CH*H*OH); 2.95 (m, 1H, C*H*CH_2OH); 2.35 (br, 5H NH_2, CH_2OH, CCH_2S); 2.11 (s, 3H, SCH_3); 1.72 (m, 1H, CC*H*C) ppm. ^{13}C NMR ($CDCl_3$), 65.96; 51.93; 32.94; 30.91; 15.39 ppm.

2.5. Preparation of (S)-2-(dimethylamino)-4-(methylthio)-1-butanol, (S)-$HOCH_2CH(NMe_2)CH_2CH_2SMe$

2.5.1. Method 1

This procedure is a modified literature preparation [3–5]. To a two-neck 500 ml round-bottomed flask equipped with a condenser, a stirring bar and a nitrogen inlet atop the condenser was added $LiAlH_4$ (5.2 g, 0.137 mol), and 150 ml of dry THF. The suspension was purged with nitrogen and cooled to 0°C. With stirring, the $HOOCCH(NMe_2)CH_2CH_2SCH_3$ (5 g, 28.2 mmol) was added in small portions over a period of 15 min. After 15 min at 0°C, the solution was allowed to warm to room temperature, stirred for an additional 15 min and then heated under reflux for 4 h under nitrogen. The reaction was cooled to 0°C and the mixture was slowly hydrolyzed by dropwise addition of water. Water was added until bubbling had subsided completely and the gray color of $LiAlH_4$ had disappeared. The white precipitates formed were removed by filtration and washed with THF. The combined filtrates were concentrated to yield a yellow liquid that was extracted into CH_2Cl_2 and the solution was washed with brine (2 × 20 ml). The solution was dried over anhydrous magnesium sulfate and the solvent removed with rotary evaporator to yield the pure product (3.82 g (66%)). ^{1}H NMR ($CDCl_3$, 25°C, 250 MHz): 3.47 (dd, 1H, C*H*HOH); 3.22 (t, 1H, CH*H*OH); 2.66 (m, 1H, C*H*CH_2OH); 2.44–2.21 (m, 2H, CH_2SCH_3); 2.22 (s, 6H, NMe_2); 2.04 (s, 3H, SCH_3); 1.77 (m 1H, C*H*HCH_2SCH_3); 1.24 (m, 1H, CH*H*CH_2SCH_3) ppm.

^{13}C NMR ($CDCl_3$); 63.92; 60.75; 40.36; 31.73; 24.65; 15.39 ppm.

2.5.2. Method 2

To a stirred solution of (*S*)-2-amino-4-(methylthio)-1-butanol (10.6 g, 79 mmol) in 50 ml of MeCN chilled in an ice bath was added a 37% solution of formaldehyde (59 ml, 790 mmol) and then this mixture was treated with $NaBH_3CN$ (14.8 g, 235 mmol) dissolved in 50 ml of MeCN. The pH of the mixture was maintained at 7 with dropwise addition of glacial acetic acid. The temperature of the solution was allowed to warm to room temperature and after 2.5 h the reaction mixture was concentrated to a golden paste which was dissolved in 50 ml of H_2O and made basic with NaOH pellets. The aqueous solution was extracted with Et_2O (1×100 ml; 5×50 ml), washed with brine (1×25 ml), dried (K_2CO_3), and concentrated to yield 12 g (92%) of a golden oil. Further purification was achieved by Kügelrohr distillation (0.35 mm; 113°C). (Spectral parameters are given in Section 2.5.1.)

2.6. Preparation of (R)-2-(dimethylamino)-3-(methylthio)-1-propanol, (R)-$HOCH_2CH(NMe_2)CH_2SCH_3$

The above procedure (method 1) was repeated with 2.83 g (74.5 mmol) of $LiAlH_4$ and 2.20 g (13.5 mmol) of $HOOCCH(NMe_2)CH_2SCH_3$, to yield 1.60 g of (*R*)-$HOCH_2CH(NMe_2)CH_2SCH_3$ (10.5 mmol (80%)), ^1H NMR ($CDCl_3$, 25°C, 250 MHz): 3.73 (dd, 1H, C*H*HOH); 3.32 (dd, 1H, CH*H*OH); 2.78 (m, 1H, C*H*CH_2OH); 2.70 (dd, 1H, C*H*HSMe); 2.31 (s, 6H, NMe_2); 2.22 (dd, 1H, CH*H*SCH_3); 2.11 (s, 3H, SCH_3).

2.7. Preparation of (S)-methophos, (S)-$Ph_2POCH_2CH(NMe_2)CH_2CH_2SCH_3$ (1)

Into a 100 ml three-necked round-bottomed flask containing a stir bar and a reflux condenser was added 0.25 g of 60% NaH. The NaH was then washed with 5×10 ml of dry pentane. Approximately 50 ml of dry THF was then added, and the flask was flushed with nitrogen. A solution of (*S*)-$HOCH_2CH(NMe_2)CH_2CH_2SCH_3$ (1.00 g, 6.14 mmol) in 5 ml of THF was added dropwise under a stream of nitrogen, and bubbling commenced. The mixture was stirred for 10 min at room temperature and then heated under reflux for 4 h under nitrogen. The color of the solution changed to a pale orange. The solution was cooled to 0°C, and Ph_2PCl (1.1 ml, 6.14 mmol) was added by syringe. The color of the solution immediately changed from orange to yellow. After stirring for 10 min at 0°C, the solution was allowed to warm to room temperature and was then stirred overnight. After the THF solvent had been removed under vacuum, 30 ml of dry diethyl ether was added via a cannula. The ether solution was transferred by cannula to a clean 100 ml flask under N_2, and 30 ml of dry hexane was added via a cannula to the ether solution, giving a pale-yellow precipitate. The clear yellow solution was carefully transferred into another flask, and the solvent was removed, yielding 1.54 g (4.41 mmol (72%)) of pure (*S*)-$Ph_2POCH_2CH(NMe_2)CH_2CH_2SCH_3$ (1) as a very-pale-yellow air-sensitive liquid. ^1H NMR ($CDCl_3$, 25°C, 250 MHz): δ7.52 (m, 4H, C_6H_5); 7.48–7.28 (m, 6H, C_6H_5); 3.91 (m, 1H, C*H*HOP); 3.84 (m, 1H, CH*H*OP); 2.82 (m, 1H, C*H*CH_2OP); 2.55 (m, 2H, CH_2SCH_3); 2.32 (s, 6H, NMe_2); 2.05 (s, 3H, SCH_3); 1.77 (m, 2H, C$H_2CH_2SCH_3$) ppm. ^{13}C NMR ($CDCl_3$): 142.1 (d, $J_{C-P} = 18$ Hz); 130.3 (d, $J_{C-P} = 6$ Hz); 130.2 (d, $J_{C-P} = 6$ Hz); 68.7 (d, $J_{C-P} = 18$ Hz); 63.2 (d, $J_{C-P} = 8$ Hz); 41.2; 31.6; 28.2; 15.3 ppm. ^{31}P NMR ($CDCl_3$): $\delta + 115.8$ ppm. Mass spectroscopy (MS) (CI): *m/z* 347 (M^+, 3%); 346 ($M^+ - H$, 7%); 201 (Ph_2PO^+, 100%). HRMS (CI). Found: 346.1396. $C_{19}H_{25}NOPS^+$, calcd.: 346.1394 for $M^+ - 1$. HRMS (electron impact) (EI). Found, 347.1477. $C_{19}H_{26}NOPS^+$, calcd.: 347.1473. The product was found to be more than 95% pure by NMR and sufficiently pure for most uses; however, it could be purified further by Kügelrohr distillation.

2.8. Preparation of (R)-cystophos, (R)-$Ph_2POCH_2CH(NMe_2)CH_2SCH_3$ (2)

The above procedure was repeated with 0.1479 g (3.7 mmol) of 60% NaH, 0.5415 g (3.7 mmol) of (*R*)-$HOCH_2CH(NMe_2)CH_2SCH_3$ and 0.65 ml (3.7 mmol) of Ph_2PCl. This gave 0.862 g (2.59 mmol (70%)) of pure (*R*)-$Ph_2POCH_2CH(NMe_2)CH_2SCH_3$ (2) as a very-pale-yellow air-sensitive liquid. ^1H NMR ($CDCl_3$, 25°C, 250 MHz): 7.50 (m, 4H, C_6H_5); 7.40–7.30 (m, 6H, C_6H_5); 4.00 (m, 2H, CH_2OP); 2.83 (m, 1H, C*H*CH_2OP); 2.64 (m, 2H, CH_2SCH_3); 2.34 (s, 6H, NMe_2); 2.07 (s, 3H, SCH_3) ppm. MS (CI). *m/z* 333 (M^+, 2%); 332 ($M^+ - H$, 5%); 201 (Ph_2PO^+, 100%). HRMS (CI). Found: 332.1240. $C_{18}H_{23}NOPS^+$ calcd.: 332.1238 for ($M^+ - H$).

2.9. Preparation of [(S)-$Ph_2POCH_2CH(NMe_2)CH_2CH_2SCH_3$] $Mo(CO)_3$ (3)

Into a 50 ml three-neck round-bottomed flask equipped with a stir bar and a condenser, $Mo(CO)_6$ (64 mg, 0.24 mmol) was suspended in 8 ml of acetonitrile. The mixture was heated under reflux until all the $Mo(CO)_6$ was converted to $Mo(CH_3CN)_3(CO)_3$, as shown by IR. After stirring for 8 h, 1.2 equivalents of (*S*)-$Ph_2POCH_2CH(NMe_2)CH_2CH_2SCH_3$ (1) (0.29 mmol; 102 μl in 2 ml CH_3CN) was added by syringe. The solution was stirred at room temperature for 4 h and then the solvent was removed under vacuum. The residue was then dissolved in 5 ml of methylene chlo-

ride, and excess pentane was added to yield a yellow precipitate. An air-sensitive yellow solid [(*S*)-$Ph_2POCH_2CH(NMe_2)CH_2CH_2SCH_3$]$Mo(CO)_3$ (**3**) (63 mg (50%)) was isolated by centrifugation and was dried under vacuum. IR (CH_2Cl_2): 1945, 1861, 1829 cm^{-1}. ^1H NMR ($CDCl_3$, 25°C, 250 MHz): 7.81–7.99 (m, 4H, C_6H_5); 7.31–7.52 (m, 6H, C_6H_5); 4.56 (m, 1H, C*H*HOP); 4.32 (m, 1H, CH*H*OP); 3.28 (m, 1H, C*H*CH_2OP); 2.83 (s, 3H, NCH_3); 2.77 (s, 3H, NCH_3); 2.74 (m, 1H, C*H*HSCH_3); 2.54 (m, 1H, CH*H*SCH_3); 2.33 (m, 1H, C*H*HCH_2SCH_3); 1.98 (m, 1H, CH*H*CH_2SCH_3); 1.92 (s, 3H, SCH_3) ppm. IR (CH_2Cl_2): 1945, 1861, 1829 cm^{-1}. MS (fast-atom bombardment (FAB)): *m/z* 529 (M^+, 34%); 501 ($M^+ - CO$, 52%); 473 ($M^+ - 2CO$, 33%). The isotope pattern of the molecular ion is identical with that calculated by computer based on the formula $C_{22}H_{26}NO_4SPMo$. HRMS. Found: 529.0300. $C_{22}H_{26}NO_4SPMo^+$ calcd.: 529.0380.

2.10. Preparation of [(R)-$Ph_2POCH_2CH(NMe_2)CH_2SCH_3$] $Mo(CO)_3$ (4)

The above procedure was repeated with 0.238 g of $Mo(CO)_6$ (0.90 mmol) and 0.300 g of (*R*)-$Ph_2POCH_2CH(NMe_2)CH_2SCH_3$ (**2**) (0.90 mmol) to give 0.320 g (0.62 mmol (69%)) of [(*R*)-$Ph_2POCH_2CH(NMe_2)CH_2SCH_3$]$Mo(CO)_3$ (**4**). IR (CH_2Cl_2): 1929, 1827, 1802 cm^{-1}. ^1H NMR ($CDCl_3$, 25°C, 300 MHz): 7.94 (m, 2H, C_6H_5); 7.70 (m, 2H, C_6H_5); 7.60 (m, 3H, C_6H_5); 7.30 (m, 3H, C_6H_5); 4.12 (dd, 2H, CH_2OPPh_2); 3.87 (m, 1H, C*H*CH_2OPPh_2); 3.64 (d, 1H, CH*H*SCH_3); 2.90 (dd, 1H, C*H*HSCH_3); 2.81 (s, 3H, NMe_2); 2.72 (s, 3H, NMe_2); 2.60 (s, 3H, SCH_3) ppm. IR (CH_2Cl_2): 1929, 1827, 1802 cm^{-1}. HRMS. Found: 515.0257. $C_{21}H_{24}NO_4SPMo^+$ calcd.: 515.0223.

2.11. Preparation of [(S)-$Ph_2POCH_2CH(NMe_2)CH_2CH_2SCH_3$]$W(CO)_3$ (5)

A 50 ml three-neck round-bottomed flask equipped with a magnetic stirrer, reflux condenser and nitrogen inlet was charged with 60 mg (0.17 mmol) of $W(CO)_6$ and 5 ml of acetonitrile. The mixture was heated under reflux for 24 h under irradiation from a UV lamp until all $W(CO)_6$ was converted to $W(CO)_3(CH_3CN)_3$, as determined by IR. The solvent was removed under vacuum and one equivalent of (*S*)-$Ph_2POCH_2CH(NMe_2)CH_2CH_2SCH_3$ (**1**) (0.17 mmol, 59 mg), in 5 ml of THF was added by cannula. The solution was stirred at room temperature for 30 min and then the solvent was removed by vacuum. The residue was dissolved in 2 ml of methylene chloride, and hexane was added to give a yellow precipitate. The yellow product was collected by filtration, washed with hexane and dried under vacuum to give 60 mg, (0.10 mmol (57%)) of [(*S*)-$Ph_2POCH_2CH(NMe_2)CH_2CH_2SCH_3$]$W(CO)_3$ (**5**). IR (CH_2Cl_2): 1923, 1820, 1791 cm^{-1}. ^1H NMR (CD_2Cl_2, 25°C, 250 MHz): 7.79–7.95 (m, 4H, C_6H_5); 7.25–7.49 (m, 6H, C_6H_5); 4.64 (ddd, 1H, C*H*HOP); 4.37 (ddd, 1H, CH*H*OP); 3.32 (m, 1H, C*H*CH_2OP); 3.02 (s, 3H, NCH_3); 2.92 (s, 3H, NCH_3); 2.86 (m, 1H, C*H*HSCH_3); 2.62 (m, 1H, CH*H*SCH_3); 2.35 (m, 1H, C*H*HCH_2SCH_3); 2.11 (s, 3H, SCH_3); 1.99 (m, 1H, CH*H*CH_2SCH_3) ppm. HRMS. Found: 615.0883. $C_{22}H_{26}NO_4SPW^+$ calc.: 615.0809.

2.12. Preparation of [η^3-(C_5H_9)Pd{(S)-$Ph_2POCH_2CHNMe_2CH_2CH_2SCH_3$}][$SbF_6$] (6)

In a 50 ml round-bottomed flask, [(η^3-1,1-dimethylallyl)PdCl]$_2$ (30 mg, 0.071 mmol) was dissolved in 10 ml of methylene chloride. Two equivalents of $AgSbF_6$ (54 mg, 0.142 mmol) in 2 ml of CH_2Cl_2 were added dropwise. A white precipitate of AgCl formed immediately. After stirring for 30 min, the solution was filtered through Celite to remove AgCl. The ligand $Ph_2POCH_2CHNMe_2CH_2CH_2SCH_3$ (47 mg, 0.13 mmol) in 5 ml of CH_2Cl_2 was added at −78°C. The solution was stirred for 30 min at −78°C and then concentrated to 2 ml. Hexane was then added to induce precipitation. The yellow product was isolated by filtration and dried under vacuum to give [η^3-(C_5H_9)Pd{(*S*)-$Ph_2POCH_2CHNMe_2CH_2CH_2SCH_3$}]-[$SbF_6$] (**6**) (70 mg (68%)). ^1H NMR (CD_2Cl_2, 25°C, 250 MHz) (note that the spectrum at this temperature is a partial average of two configurations of the allyl): 7.75–7.31 (m, 10H); 5.39 (br t, 1H, HC allyl); 4.28 (br s, 1H, OC*H*H); 4.18 (br s, 1H, OCH*H*); 2.9–2.6 (vbr m, 6H); 2.80 (s, 6H, NMe_2); 2.2 (br, 2H); 2.18 (br s, 3H, SMe); 2.01 (br d, 3H, CMe); 1.60 (vbr s, 2H, CHH) ppm. ^{31}P NMR ($CDCl_3$, 25°C, 121 MHz): 128.3 ppm. MS (FAB): *m/z* 522 ([$C_5H_9PdPh_2POCH_2CHNMe_2CH_2CH_2SCH_3$]$^+$, 100%). The isotope pattern of the molecular cation is identical with that calculated by computer based on the formula $C_{24}H_{35}NOSPPd$. HRMS (FAB). Found: 522.1240. $C_{24}H_{35}NOSPPd$ calcd.: 522.1209. Anal. Found: C, 37.12; H, 4.49; N 1.77; S, 4.13. $C_{24}H_{35}NOSPPdSbF_6$ calcd.: C, 37.99; H, 4.65; N, 1.85; S, 4.23%.

2.13. Preparation of [η^3-(C_4H_7)Pd{(R)-$Ph_2POCH_2CHNMe_2CH_2SCH_3$}][$SbF_6$] (7)

The above procedure was repeated with 0.121 g (0.31 mmol) of [(η^3-2-methallyl)PdCl]$_2$, 0.210 g (0.61 mmol) of $AgSbF_6$ and 0.204 g (0.61 mmol) of (*S*)-$Ph_2POCH_2CHNMe_2CH_2SCH_3$) which gave 0.298 g (0.41 mmol, 67%) of pure [η^3-(C_4H_7)Pd{(*R*)-$Ph_2POCH_2CHNMe_2CH_2SCH_3$}][$SbF_6$] (**7**). ^1H NMR ($CDCl_3$, 25°C, 300 MHz): 7.80–7.35 (m, 10H); 4.38 (br

TABLE 1. Crystallographic data for X-ray diffraction studies of [(*S*)-methophos]W(CO)$_3$

Crystal parameters	
Formula	$WPSNO_4C_{22}H_{26}$
Space group	$P2_1$ (No. 4)
a (Å)	8.8435(6)
b (Å)	14.384(1)
c (Å)	9.546(1)
β (°)	107.051(8)
V (Å^3)	1161.0(4)
Formula weight	615.4
ρ_{calc} (g cm^{-3})	1.760 ($Z = 2$)
Absorption coefficient (cm^{-1})	52.61
Crystal dimensions (mm × mm × mm)	0.28 × 0.25 × 0.18
T (°C)	23
Intensity measurements	
Diffractometer	Enraf–Nonius CAD4
Monochromator	Graphite
Radiation	Mo Kα (λ = 0.710 73 Å)
Reflections measured	$+h, +k, \pm l$
Maximum 2θ (°)	52
Number of reflections measd	2376
Solution and refinement	
Number of data used, $F^2 > 2\sigma(F^2)$	2018
Number of parameters refined	270
Absorption correction	DIFABS (0.76–1.00 transmission)
p factor	0.01
Final residuals R; R_w	0.020; 0.021
Goodness-of-fit indicator	1.40
Maximum shift/error in final cycle	0.00
Largest peak in final difference map (electrons Å^{-3})	0.41

m, 2H, CH_2O); 3.12 (br s, 2H); 2.95 (br s, 1H); 2.59 (s, 3H, MeC); 2.48 (s, 6H, NMe$_2$); 2.38 (m, 1H); 2.09 (m, 1H); 2.02 (s, 3H, SMe); 0.88 (m, 1H); 0.11 (m, 1H) ppm. ^{31}P NMR ($CDCl_3$, 25°C, 121 MHz): 135.1 ppm. HRMS (FAB). Found: 494.0890. $C_{24}H_{35}NOSPPd$ calcd.: 494.0896.

2.14. The X-ray crystal structure of 5

A yellow crystal of **5** suitable for X-ray diffraction analysis was grown from CH_2Cl_2 and hexane and mounted in a glass capillary. A summary of the data collection is given in Table 1. The unit-cell parameters were determined by least-squares refinement of the setting angles of 25 large-angle reflections. The data were corrected for Lorentz and polarization effects. Three standard reflections were monitored throughout the data collection and showed no loss of intensity (average variation, 0.5%). Absorption corrections were made using the program DIFABS [6] which calculated transmission factors of 0.86–1.18. ψ scans indicated a range of transmission factors from 0.76 to 1.00.

All calculations were carried out using the TEXSAN 5.1 software package [7] run on VAXstation 3100 and 4000 computers. The structure was solved using Patterson heavy-atom methods to locate the tungsten atom and subsequent difference Fourier techniques. Hydrogen atoms were included in calculated positions and non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement converged with agreement factors of $R = 0.020$ and $R_w = 0.021$. The absolute configuration was determined by reference to the known configuration of the (S_C)-methionine. This was confirmed by the increase in agreement factors upon refinement of the (R_C) enantiomer ($R = 0.027$ and $R_w = 0.032$). The final positional parameters are given in Table 2 and relevant bond distances and angles in Tables 3 and 4, respectively. Complete tables of the crystallographic data (anisotropic thermal parameters, hydrogen atom coordinates and structure factors) may be obtained from one of the authors (J.W.F.).

TABLE 2. Positional parameters and B_{eq} for [(*S*)-methophos]W(CO)$_3$

Atom	x	y	z	B_{eq} (Å^2)
W	0.98275(3)	0.9924	0.19425(2)	2.891(9)
S	0.9534(2)	0.9675(1)	0.4499(2)	3.53(8)
P	0.7044(2)	1.0484(1)	0.1095(2)	2.62(6)
O(1)	1.3309(8)	0.9223(5)	0.3209(7)	6.5(3)
O(2)	1.1351(7)	1.1862(4)	0.2870(7)	5.7(3)
O(3)	1.0611(7)	1.0147(8)	−0.1013(6)	7.2(4)
O(4)	0.5821(6)	0.9803(5)	0.1569(5)	3.6(2)
N	0.8653(8)	0.8415(4)	0.1530(7)	4.0(3)
C(1)	1.199(1)	0.9459(6)	0.2735(8)	4.0(3)
C(2)	1.0734(9)	1.1145(6)	0.2472(8)	3.7(3)
C(3)	1.0272(8)	1.008(1)	0.0104(7)	4.1(4)
C(4)	0.769(1)	0.9129(6)	0.4512(8)	4.4(4)
C(5)	0.739(1)	0.8237(6)	0.366(1)	5.8(5)
C(6)	0.719(1)	0.8251(7)	0.199(1)	4.0(4)
C(7)	0.578(1)	0.8827(5)	0.1175(9)	3.9(3)
C(8)	0.927(1)	1.0784(6)	0.5278(8)	4.6(4)
C(9)	0.984(1)	0.7710(7)	0.225(1)	7.1(5)
C(10)	0.827(1)	0.8214(7)	−0.008(1)	5.9(4)
C(11)	0.655(1)	1.1558(6)	0.191(1)	2.8(3)
C(12)	0.535(1)	1.1625(5)	0.2547(8)	3.7(3)
C(13)	0.509(1)	1.2432(6)	0.3187(9)	4.7(4)
C(14)	0.604(1)	1.3198(7)	0.322(1)	5.3(4)
C(15)	0.724(1)	1.3138(6)	0.256(1)	4.7(4)
C(16)	0.748(1)	1.2343(6)	0.1914(8)	4.0(3)
C(17)	0.5999(8)	1.0700(5)	−0.0835(6)	2.9(3)
C(18)	0.440(1)	1.0512(5)	−0.1362(9)	4.2(3)
C(19)	0.360(1)	1.0660(6)	−0.283(1)	5.8(4)
C(20)	0.440(1)	1.1008(7)	−0.3750(9)	5.8(5)
C(21)	0.596(1)	1.1242(9)	−0.3228(9)	6.4(5)
C(22)	0.677(1)	1.1053(8)	−0.1795(9)	5.4(4)

TABLE 3. Intramolecular distances for [(*S*)-methophos]W(CO)$_3$

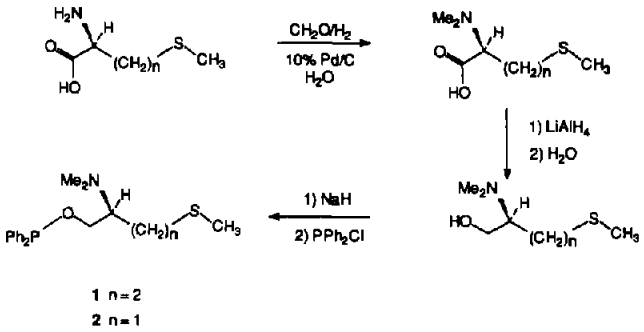
Atom	Atom	Distance (Å)	Atom	Atom	Distance (Å)
W	S	2.554(2)	N	C(10)	1.50(1)
W	P	2.489(2)	C(4)	C(5)	1.50(1)
W	N	2.389(7)	C(5)	C(6)	1.55(1)
W	C(1)	1.959(8)	C(6)	C(7)	1.51(1)
W	C(2)	1.935(8)	C(11)	C(12)	1.38(1)
W	C(3)	1.922(7)	C(11)	C(16)	1.40(1)
S	C(4)	1.814(8)	C(12)	C(13)	1.36(1)
S	C(8)	1.802(8)	C(13)	C(14)	1.38(1)
P	O(4)	1.619(6)	C(14)	C(15)	1.39(1)
P	C(11)	1.839(9)	C(15)	C(16)	1.35(1)
P	C(17)	1.829(6)	C(17)	C(18)	1.38(1)
O(1)	C(1)	1.169(9)	C(17)	C(22)	1.39(1)
O(2)	C(2)	1.177(9)	C(18)	C(19)	1.39(1)
O(3)	C(3)	1.193(8)	C(19)	C(20)	1.37(1)
O(4)	C(7)	1.45(1)	C(20)	C(21)	1.37(1)
N	C(6)	1.50(1)	C(21)	C(22)	1.37(1)
N	C(9)	1.47(1)			

3. Results and discussion

We have prepared the tridentate ligands **1** and **2** from their corresponding amino acids via methylation of the amino moiety, reduction with $LiAlH_4$ to give the dimethylated amino alcohol, and deprotonation of the alcohol followed by addition of PPh_2Cl (Scheme 1). The synthesis of the alcohol is precedented in literature procedures, but we initially encountered some difficulties in the methylation reaction. The problems

TABLE 4. Selected intramolecular bond angles for [(*S*)-methophos]W(CO)$_3$

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
S	W	P	89.32(6)	O(4)	P	C(17)	101.7(3)
S	W	N	82.5(2)	C(11)	P	C(17)	99.9(3)
S	W	C(1)	86.8(2)	P	O(4)	C(7)	118.8(4)
S	W	C(2)	91.6(2)	W	N	C(6)	117.7(5)
S	W	C(3)	174.2(2)	W	N	C(9)	109.4(5)
P	W	N	84.2(2)	W	N	C(10)	107.4(5)
P	W	C(1)	176.1(2)	C(6)	N	C(9)	108.3(7)
P	W	C(2)	94.9(2)	C(6)	N	C(10)	108.4(7)
P	W	C(3)	96.5(2)	C(9)	N	C(10)	104.8(7)
N	W	C(1)	94.7(3)	W	C(1)	O(1)	177.0(8)
N	W	C(2)	174.0(3)	W	C(2)	O(2)	175.8(7)
N	W	C(3)	98.8(4)	W	C(3)	O(3)	176.6(9)
C(1)	W	C(2)	85.7(3)	S	C(4)	C(5)	112.3(6)
C(1)	W	C(3)	87.4(3)	C(4)	C(5)	C(6)	119.8(7)
C(2)	W	C(3)	87.2(4)	N	C(6)	C(5)	116.8(8)
W	S	C(4)	114.2(2)	N	C(6)	C(7)	114.7(8)
W	S	C(8)	109.3(3)	C(5)	C(6)	C(7)	111.4(9)
C(4)	S	C(8)	99.0(4)	O(4)	C(7)	C(6)	116.3(7)
W	P	O(4)	113.1(2)	P	C(11)	C(12)	123.7(7)
W	P	C(11)	117.9(3)	P	C(11)	C(16)	117.9(7)
W	P	C(17)	122.8(2)	P	C(17)	C(18)	119.6(5)
O(4)	P	C(11)	97.5(4)	P	C(17)	C(22)	121.9(6)

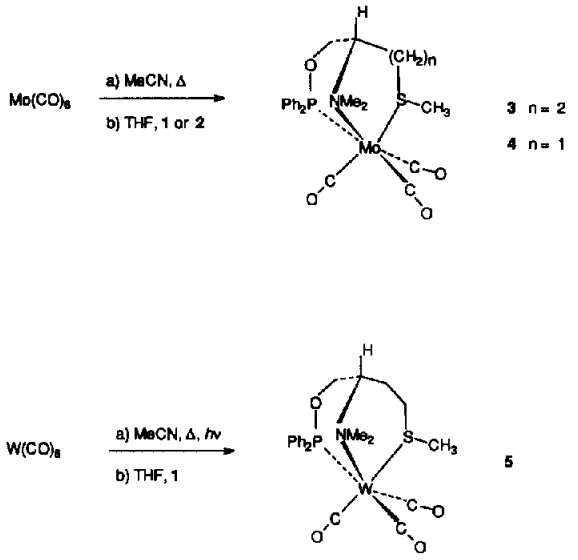


Scheme 1.

with variability of yield in this reaction were eventually overcome by vigorously bubbling H_2 through the mixture before allowing the reaction to stand. We also developed an alternative route in which the amino acid was first reduced to the alcohol and subsequently the amine was methylated. The original method appears to give a slightly purer product and the complexes reported here were made from ligands prepared by that route. For convenient reference, we have abbreviated the names of these compounds to (*S*)-methophos for **1** and (*R*)-cystophos for **2**. In addition to the difference in donor character and enhanced back-bonding capacity of the phosphorus, the phosphinito compounds **1** and **2** differ from the known phosphine-containing Kellogg ligands by having an additional atom in the linkage to the amino carbon which changes the ring size of one of the chelates, making it more flexible and potentially allowing accommodation of a greater range of complex formation and stabilities.

The metal complexes of W and Mo were prepared from the metal hexacarbonyls, via the trisacetonitrile complexes $M(CO)_3(AN)_3$ and reaction with **1** or **2** in THF (Scheme 2). The carbonyl stretching bands in the IR spectra show a classic three-band pattern attributable to a *fac* tricarbonyl. The lack of acetonitrile in the products suggested that the ligands were bound in a tridentate fashion. The X-ray crystal structure determination of **5** confirms the facial arrangement and shows that ligand **1** is indeed tridentate or η^3.

The Pd complexes **6** and **7** were prepared from the corresponding $[(allyl)PdCl]_2$, dimer by reaction with $AgSbF_6$, and addition of L to give the $LPd(allyl)SbF_6$ complex (Scheme 3). The ^1H NMR spectra exhibit downfield shifts for the N methyl resonances, and a change in shifts for the P phenyls, compared with the free ligand. There is virtually no change in the S methyl resonance. The absence of coordination shifts for the S methyl in each of these positively charged complexes indicates that the ligands are bidentate with the P and N binding, and have a free S donor. The ^1H NMR spectrum also compares favorably with the Kel-



Scheme 2.

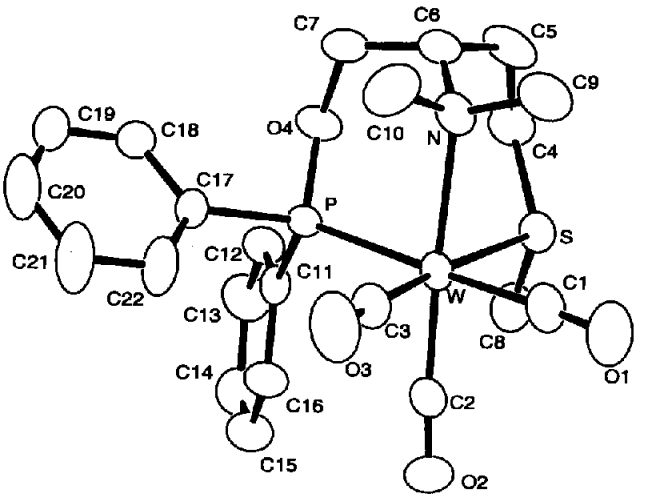
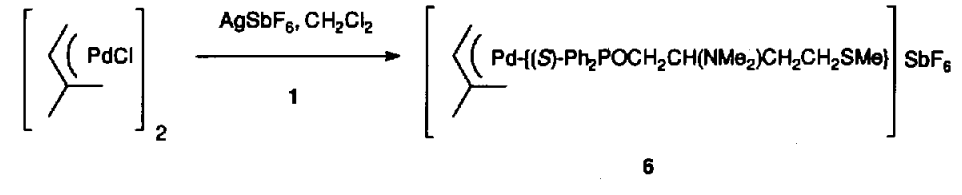


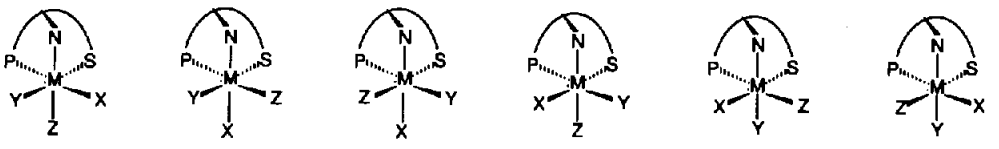
Fig. 1. An ORTEP view of (*S*)-methophos $W(CO)_3$ with 50% thermal ellipsoids.

logg complexes [4] $LPdCl_2$ (where L is $Ph_2PCH_2CH(NMe_2)(CH_2)_{-n}SMe$), that are known by X-ray crystallography to be bidentate with P and N chelating. The coordination shift observed for the ^{31}P NMR resonance also shows that the P atom is bound to the metal.

The X-ray structure of **5** is shown in Fig. 1 and relevant metrical data are given in Tables 3 and 4. The Kellogg phosphine ligand derived from methionine in the bidentate complex has a P–Pd–N bite angle of 86.9°, whereas for **5** which contains (*S*)-methophos it has a P–W–N bite angle of 84.2°. The longer bond lengths for W^0 compared with Pd(II) (*e.g.* a W–P length of 2.489 Å *vs.* a Pd–P length of 2.214 Å) are compensated by the increase in chelate ring size. Of particular importance in this structure is the *trans* influence exhibited by the P, N and S donors on the W–C bond lengths. These W–C bond distances of 1.959(8), 1.935(8) and 1.922(7) Å and corresponding C–O distances of 1.169(9), 1.177(9) and 1.193(8) Å *trans* to P, N and S illustrate this important effect. The W–C bond *trans* to P differs significantly from that *trans* to S. The other distances reflect the trend, al-



Scheme 3.



Scheme 4.

though the middle values might be considered to be too close to either of the end values to have a high confidence level in their significance. This *trans* influence is also observed in the exceptionally wide spread of the C≡O stretching frequencies (1923, 1820 and 1791 cm^{-1}), although some of this separation is attributable to stretch–stretch interaction force constants. One would expect that these differences would also be reflected in the relative ease of displacement of the ligands *trans* to the various donors. We expect that these ligands with three different donors should thus be able to effectively control the preferred arrangement of ligands *trans* to the specific donors, if the remaining ligands had substantially different donor and/or acceptor character, as well. Thus, depending upon the relative preference for X, Y or Z to be *trans* to P, N or S, the ligand should produce a strong thermodynamic bias for one isomer of the six that are possible (Scheme 4). In principle, this should be very important in assembling reactants in a catalytic intermediate (see Scheme 4) since, if the X, Y and Z were removed in a reaction, a new X, Y and Z set would reassemble to the same stable structure. We are currently investigating the potential for using this approach for stereocontrolled synthesis of LMXYZ octahedral systems.

The ^{1}H NMR spectra of a ligand such as **5** would be expected to be rather complicated since all the methylene protons are rendered diastereotopic by the chirality. Further complications can arise in the complexes owing to stereochemical non-rigidity in either the ligand itself and/or the other ligands. The sulfur is prochiral and two diastereomers are feasible upon binding. The crystal structure of **5** shows the configuration at sulfur to be (S_S). Rapid inversion at sulfur in metal-dialkyl sulfide complexes is a well-documented phenomena [8–11] with barriers generally in the range 9–13 kcal mol^{-1}. These barriers are often not sufficiently low to prevent broadening in room-temperature spectra, particularly those obtained with high field NMR spectrometers. One can also anticipate barriers to conformational rearrangement in the rings causing broadening at lower temperatures. In **4** and **5** the ring conformation rearrangements and the $(S_S) \rightleftharpoons (R_S)$ interconversion rates are sufficiently fast that the spectra have averaged to yield relatively easily interpreted spectra. In complexes with asymmetrical ligands such as **6**, isomerism at sulfur and the orientation of the dimethylallyl ligand produces eight possible isomers. Since $\eta^3 \rightleftharpoons \eta^1 \rightleftharpoons \eta^3$ of the allyl occurs, interpretation of the ^{1}H NMR at room temperature can be quite a challenge and ^{1}H NMR is of marginal use in routine characterization.

4. Conclusion

We have prepared two new chiral tridentate ligands from inexpensive, readily available amino acids, as well as several metal complexes which may be prove useful as homogeneous asymmetric catalysts. The crystal structure of **5**, as well as the IR and NMR spectra of **3**–**5** prove that **1** and **2** have the ability to bind as tridentate ligands, and they have created a very asymmetric electronic environment about the metal. We are currently studying these ligands as catalyst poisons in hydrogenations, and complexes of these ligands as potential homogeneous catalysts in a variety of asymmetric syntheses.

Acknowledgments

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