DALTON

Chiral oxazoline ligands. Synthesis and characterization of palladium, nickel and manganese complexes containing bidentate N,O and N,P moieties †

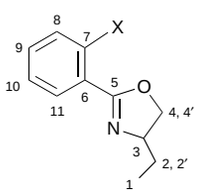
Montserrat Gómez-Simón,*[a] Susanna Jansat,[a] Guillermo Muller,*[a] David Panyella,[a] Mercè Font-Bardía[b] and Xavier Solans[b]

[a] *Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès, 1-11, 08028 Barcelona, Spain*
[b] *Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028 Barcelona, Spain*

Complexes of palladium, nickel and manganese, with the chiral ligand (+)-(4′*R*)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)phenol HL^{OH} were synthesized and characterized by ^{1}H, ^{31}P NMR spectroscopy, magnetic susceptibility and including the crystal structure determinations of *trans*-$[PdL^{OH}_2]$ and $[PdClL^{OH}(PPh_3)]$. The L^{OH} moiety is co-ordinated in a bidentate fashion in neutral, cationic and anionic complexes, rigid on the NMR time-scale. Monodentate *O*-co-ordinated complexes were obtained only in the presence of phosphines. The manganese complex $[MnClL^{OH}_2]$ showed little activity in the catalytic epoxidation of styrene. The first phosphinite oxazoline ligand L^{OP} was synthesized from HL^{OH}. Neutral and cationic alkyl and allyl complexes of palladium with it were obtained and characterized. The cationic complexes showed dynamic behaviour.

The use of oxazoline ligands as chirality-transfer auxiliaries in a wide range of catalytic reactions has been widely reported in recent years. In particular, oxazolines have been used as chiral auxiliaries, either alone or as arms in polyfunctional ligands, in combination with several transition metals in allylic substitutions,[1] allylic amminations,[2] alkene or ketone hydrosilylations,[3,4] alkene cyclopropanations,[5] Diels–Alder reactions,[6] copolymerization reactions,[7] epoxidations of olefins,[8] Heck reactions[9] and sulfide reactions.[10] However, studies of the transition-metal complexes containing the oxazoline groups, catalyst precursors of the active species, are still highly limited, either from the point of view of their preparative chemistry or reactivity patterns. Several studies have been published on this aspect, above all in the field of allyl complexes[11] and their complexity has recently been demonstrated by Sprinz *et al.*[12] Yang *et al.*[13,14] reported a group of palladium compounds containing chiral N,O-chelates. Kurosawa and co-workers[15] have studied the distribution of diastereomers in η^3-allylbis(oxazoline)palladium compounds which appear to be the intermediate species in the allylic substitution reaction. Also, Floriani and co-workers[16] prepared a number of chiral neutral and cationic alkylzirconium complexes that could be used as precursors of polymerization catalysts.

The oxazoline group alone or in combination with other functionalities such as phosphine or pyridine type fragments could be achieved in several ways.[17] However, phosphinite–oxazoline ligands have not previously been described in the literature. The preparation of the oxazoline fragment by reaction between aminoalcohols and nitriles is an attractive method since both types of compounds are commercially available including a number of accessible enantiomerically pure aminoalcohols. By using this synthetic procedure it is possible to change the size of the substituents at the chiral carbon of the oxazoline and therefore to achieve some modulation of the asymmetric induction provided by the ligand.



X = OH (HL^{OH}), $OPPh_2$ (L^{OP})

Although the control of the stereoselectivity of the catalytic processes with complexes containing two analogous oxazoline moieties is mainly steric,[18] some modulation with the contribution of electronic factors could be possible, as has also been theoretically proposed, using ligands with mixed fragments (N–O, N–P . . .).[19] It is necessary, therefore, to further our understanding of the kind of isomers present in solid state and in solution and of their interconversion processes, so that we might discuss the stereoselectivity of the catalytic reactions.

This paper describes the preparation of mono(oxazoline) bidentate ligands HL^{OH} and L^{OP} and the synthesis of palladium, nickel and manganese chiral complexes, which can be potential catalytic precursors or intermediates in catalytic processes. The solid-state and solution structure of the anionic and neutral complexes prepared are discussed. Also, the results of the catalytic epoxidation of styrene with the manganese(III) compound are described.

Experimental

General

All compounds were prepared under a purified nitrogen atmosphere using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures[20] and distilled under nitrogen. L-(−)-2-Aminobutanol (Janssen) was used without previous purification. Zinc chloride (Merck) was purified following a classical procedure.[20] Sodium hypochlorite (10%) was obtained from Panreac, Aliquat 336 and octylbenzene (standard for GC) from Aldrich and Fluka. Sytrene (Fluka) was distilled immediately before use. Styrene oxide and *R*-(−)-styrene oxide were from Aldrich.

† *Supplementary data available* (No. SUP 57274, 2 pp.): the EPR spectrum of complex **12a**. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997.

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

The NMR spectra were recorded on Varian XL-500 (^{1}H, standard $SiMe_4$), Unity 300 (^{19}F, 282 MHz, standard $CFCl_3$), Varian Gemini (^{13}C, 50 MHz, standard $SiMe_4$) and Bruker DRX 250 (^{31}P, 101 MHz, standard H_3PO_4) spectrometers. Chemical shifts are reported downfield from standards. The IR spectra were recorded on a Nicolet 520 FT-IR spectrometer. The FAB mass chromatograms were obtained on a Fisons V6-Quattro instrument, GC–mass spectrometric analysis on a Hewlett-Packard 5890 Series II gas chromatograph (50 m Ultra 2 capillary column) interfaced to a Hewlett-Packard 5971 mass-selective detector. Product analyses of catalytic reactions were conducted on a Hewlett-Packard 5890 Series II gas chromatograph with either a 30 m Carbowax capillary column or a 25 or 50 m FS-Cyclodex β-I/P capillary column. Magnetic measurements were carried out at variable temperature (300–4 K) on polycrystalline samples with a pendulum-type magnetometer (Manics DSM8) equipped with a Drusch EAF 16 UE electromagnet. The magnetic field was approximately 1.5 T. Diamagnetic corrections were estimated from Pascal's tables. Optical rotations were measured at 25 °C at the sodium D line on a Perkin-Elmer 241MC spectropolarimeter. Conductivities were obtained on a Radiometer CDM3 conductimeter. Elemental analyses were carried out by the Serveis Científico-Tècnics of the Universitat de Barcelona in an Eager 1108 microanalyser.

Preparations

(+)-(4′*R*)-2-(4′-Ethyl-3′,4′-dihydrooxazol-2′-yl)phenol, HL^{OH}. This compound was synthesized following a published procedure[21] with certain modifications. L-(−)-2-Aminobutanol (1.64 g, 18.40 mmol), 2-hydroxybenzonitrile (1.83 g, 15.40 mmol) and $ZnCl_2$ (52.5 mg, 0.385 mmol) were dissolved in toluene (25 cm^3) and refluxed for 72 h under nitrogen. The reaction mixture was filtered off and distilled *in vacuo*, affording a yellow oil (2.30 g, 78%), which was purified by flash chromatography (ethyl acetate). $[\alpha]_D^{25} = +52.3°$ (*c* 0.1, $CHCl_3$).

(4′*R*)-1-(Diphenylphosphanyloxy)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)benzene L^{OP}. To a solution of compound HL^{OH} (2.10 g, 11 mmol) and triethylamine (1.11 g, 11 mmol) in toluene (20 cm^3) was added dropwise chlorodiphenylphosphine (2.43 g, 11 mmol) in 10 cm^3 of the same solvent at −78 °C. The mixture was stirred for 6 h while the solution was warmed gradually to room temperature. The white precipitate was filtered off and the solution concentrated under reduced pressure to yield a dark orange oil. This was dissolved in diethyl ether (20 cm^3) and washed with degassed water (3 × 10 cm^3). The organic phase was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under reduced pressure to yield an orange oil, L^{OP} (2.97 g, 72%).

***trans*-Bis[(4′*R*)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)phenolato-*N*,*O*]palladium(II) 1a.** To a solution of $Pd(O_2CMe)_2$ (0.23 g, 1.05 mmol) in dichloromethane (10 cm^3) was added a solution of HL^{OH} (0.40 g, 2.10 mmol) in 5 cm^3 of the same solvent. The solution was stirred at room temperature for 2 h, then concentrated to *ca.* 5 cm^3 and hexane added. Orange crystals (0.38 g, 78%) were separated after keeping the solution in a freezer for 2 d. M.p. (decomp.) = 145 °C (Found: C, 53.8; H, 4.92; N, 5.85. Calc. for $C_{22}H_{24}N_2O_4Pd$: C, 54.28; H, 4.97; N, 5.75%).

Chloro[(4′*R*)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)phenolato-*N*,*O*](triphenylphosphine)palladium(II) 2a. The complex $[PdCl(acac)(PPh_3)]$[22] (acac = acetylacetonate) (0.40 g, 0.80 mmol) and HL^{OH} (0.16 g, 0.80 mmol) were dissolved in toluene (20 cm^3) at −78 °C. The mixture was warmed at room temperature, stirred for 6 h, then concentrated under reduced pressure, affording an orange solid. The product was recrystallized from toluene and hexane, yielding orange crystals, which contained toluene (0.35 g, 64%). M.p. = 86 °C (Found: C, 63.00; H, 5.27; N, 2.30. Calc. for $C_{29}H_{27}ClNO_2PPd\cdot C_7H_8$: C, 62.98; H, 5.14; N, 2.04%). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 26.0.

[2-(Benzyliminomethyl)phenyl-*C*,*N*][(4′*R*)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)phenolato-*N*,*O*]palladium(II) 3a. The cyclometallated complex $[\{Pd(C_6H_4CH{=}NCH_2Ph)(\mu\text{-}O_2CMe)\}_2]$[23] (0.21 g, 0.30 mmol) and HL^{OH} (0.12 g, 0.60 mmol) were dissolved in dichloromethane (15 cm^3) and stirred at room temperature for 3 h. The reaction mixture was then concentrated under reduced pressure, affording a yellow solid which was recrystallized from dichloromethane and diethyl ether (0.21 g, 70%). M.p. (decomp.) = 135 °C (Found: C, 61.26; H, 4.73; N, 5.74. Calc. for $C_{25}H_{23}N_2O_2Pd$: C, 61.15; H, 4.93; N, 5.72%).

[2-(2-Methoxyphenyliminomethyl)-4,5-dimethoxyphenyl-*C*,*N*][(4′*R*)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)phenolato-*N*,*O*]palladium(II) 4a. The cyclometallated complex $[\{Pd[3,4\text{-}(MeO)_2C_6H_2CH{=}NC_6H_4OMe\text{-}2](\mu\text{-}O_2CMe)\}_2]$[24] (0.09 g, 0.10 mmol) and HL^{OH} (0.04 g, 0.20 mmol) were dissolved in toluene (15 cm^3) and stirred at room temperature for 6 h. The reaction mixture was then concentrated under reduced pressure, affording an orange oil. The residue was dissolved in dichloromethane (10 cm^3) and hexane added. After keeping the solution in a freezer overnight a yellow solid (0.10 g, 85%) was separated. M.p. (decomp.) = 173 °C (Found: C, 57.20; H, 4.85; N, 4.65. Calc. for $C_{27}H_{28}N_2O_5Pd$: C, 57.20; H, 4.98; N, 4.94%).

[(4′*R*)-2-(4′-Ethyl-3′,4′-dihydrooxazol-2′-yl)phenolato-*N*,*O*]-(2,4,6-trimethylphenyl)(triphenylphosphine)palladium(II) 5a. *n*-Butyllithium (0.28 cm^3, *ca.* 1.6 M, 0.44 mmol) in hexane was added to a solution of HL^{OH} (0.086 g, 0.44 mmol) in tetrahydrofuran (10 cm^3) at −78 °C. After 30 min the lithium oxazolinato solution was added to a solution of $[\{Pd(C_6H_2\text{-}Me_3\text{-}2,4,6)(PPh_3)(\mu\text{-}Br)\}_2]$[25] (0.24 g, 0.22 mmol) in thf (10 cm^3). After stirring for 12 h, the mixture was concentrated under reduced pressure, affording an orange solid. The product was recrystallized from toluene and hexane (0.20 g, 65%). M.p. (decomp.) = 110 °C (Found: C, 66.90; H, 5.93; N, 2.10. Calc. for $C_{38}H_{38}NOPPd$: C, 67.31; H, 5.65; N, 2.07%). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 27.3.

***trans*-Bis(dimethylphenylphoshine)bis[(4′*R*)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)phenolato-*N*,*O*]palladium(II) 6a.** To a solution of compound **1a** (0.11 g, 0.22 mmol) in CH_2Cl_2 (20 cm^3) was added a solution of dimethylphenylphosphine (0.09 g, 0.66 mmol) at −75 °C. The mixture was warmed at room temperature, stirred for 2 h, then concentrated under reduced pressure, affording a yellow solid which was recrystallized from dichloromethane and diethyl ether (0.13 g, 78%). M.p. = 135 °C (Found: C, 59.50; H, 5.90; N, 3.52. Calc. for $C_{38}H_{46}N_2O_4P_2Pd$: C, 59.81; H, 6.08; N, 3.67%). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 33.8.

[(4′*R*)-2-(4′-Ethyl-3′,4′-dihydrooxazol-2′-yl)phenolato-*N*,*O*]-(η^3-2-methylallyl)palladium(II) 7a. To a solution of di(μ-chloro)-bis(η^3-2-methylallyl)dipalladium[26] (0.25 g, 0.63 mmol) in CH_2Cl_2 (20 cm^3) was added a solution of HL^{OH} (0.12 g, 1.26 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) (0.19 g, 1.26 mmol) in 10 cm^3 of the same solvent. The mixture was refluxed for 2 h. After cooling at room temperature, the solution was concentrated to *ca.* 15 cm^3 under reduced pressure and hexane added. A pale yellow solid (0.25 g, 57%) separated after keeping the solution in a freezer overnight. M.p. (decomp.) = 140 °C (Found: C, 51.00; H, 5.30; N, 4.10. Calc. for $C_{15}H_{19}NO_2Pd$: C, 51.22; H, 5.45; N, 3.98%).

(η^3-Allyl)[(4′*R*)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)phenolato-*N*,*O*]palladium(II) 8a. Complex **8a** was prepared by the same procedure as described above from bis(η^3-allyl)di(μ-bromo)-

dipalladium[26] (0.29 g) as a yellow solid (0.26 g, 61%). M.p. (decomp.) = 120 °C. (Found: C, 49.68; H, 4.88; N, 4.00. Calc. for $C_{14}H_{17}NO_2Pd$: C, 49.79; H, 5.07; N, 4.15%).

Bis[(4′*R*)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)phenolato-*N*,*O*]nickel(II) 9a. To a solution of $Ni(O_2CMe)_2$ (0.60 g, 3.40 mmol) in tetrahydrofuran (15 cm^3) was added a solution of HL^{OH} (2.0 g, 10.50 mmol) in 10 cm^3 of the same solvent. The solution was stirred at room temperature overnight. The mixture was then concentrated to *ca.* 10 cm^3 and hexane (15 cm^3) added. A dark green solid (1.0 g, 67%) separated after keeping the solution in a freezer overnight. M.p. (decomp.) = 110 °C (Found: C, 59.98; H, 5.56; N, 6.24. Calc. for $C_{22}H_{24}N_2NiO_4$: C, 60.17; H, 5.51; N, 6.38%).

[(4′*R*)-2-(4′-Ethyl-3′,4′-dihydrooxazol-2′-yl)phenolato-*N*,*O*](2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene)nickel(II) perchlorate 10a. The compound $[\{NiL(\mu\text{-}OH)\}_2][ClO_4]_2$[27] (L = 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene) (0.45 g, 0.628 mmol) and HL^{OH} (0.240 g, 1.25 mmol) were dissolved in dichloromethane (20 cm^3) at room temperature and then warmed at reflux temperature for 1 h. At room temperature a green solid was obtained after the addition of hexane (20 cm^3). The product was filtered off and recrystallized from dichloromethane and hexane (0.60 g, 83.3%). M.p. = 180 °C (Found: C, 49.80; H, 6.53; N, 9.69. Calc. for $C_{24}H_{39}ClN_4NiO_6$: C, 50.24; H, 6.85; N, 9.76%). Positive-ion FAB mass spectrum: *m*/*z* 475 (*M* + 1, 73), 474 (*M*, 39), 473 (*M* − 1, 100%), 307 (28), 284 (24), 283 (40.5), 282 (51.4) and 281 (31%). Λ_M = 148 S cm^2 mol^{-1} (acetonitrile, 8.8×10^{-4} M).

Tetraethylammonium [(4′*R*)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)phenolato-*N*,*O*]bis(pentafluorophenyl)nickel(II) 11a. The salt $[NEt_4]_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]$[28] (0.16 g, 0.148 mmol) and HL^{OH} (0.057 g, 0.296 mmol) were dissolved in dichloromethane (5 cm^3) and stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure, affording a yellow oil. The residue was washed with diethyl ether and dissolved in dichloromethane (5 cm^3) and hexane (20 cm^3). A yellow solid was obtained after cooling the solution in a refrigerator overnight. The product was filtered off, washed with hexane, and dried under reduced pressure (0.17 g, 80.5%). M.p. (decomp.) = 138 °C (Found: C, 52.00; H, 4.85; N, 4.02. Calc. for $C_{31}H_{32}F_{10}N_2NiO_2$: C, 52.19; H, 4.52; N, 3.93%). Negative-ion FAB mass spectrum: *m*/*z* 584 (*M* + 1, 42), 582 (*M* − 1, 100), 391 (24) and 315 (11%). Λ_M = 130 S cm^2 mol^{-1} (acetone, 8.8×10^{-4} M). ^{19}F NMR ($CDCl_3$): δ −122.1 (1 F_o, m), −123.9 (2 F_o, m), −125.3 (1 F_o, m), −170.1 [1 F_p, t, ^3J(FF) 19.8], −171.5 [1 F_p, t, ^3J(FF) 19.8 Hz], −172.4 (3 F_m, m) and −173.4 (1 F_m, m).

Bis[(4′*R*)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)phenolato-*N*,*O*]manganese(II) 12a. To a solution of $Mn(O_2CMe)_2{\cdot}4H_2O$ (0.64 g, 2.61 mmol) in absolute ethanol (20 cm^3) was added a solution of HL^{OH} (1.00 g, 5.23 mmol) in 10 cm^3 of the same solvent. The solution was concentrated under reduced pressure, affording a dark oil. The residue was treated with diethyl ether and hexane. A green solid was obtained after cooling the solution in a refrigerator overnight, filtered off, washed with hexane and dried under reduced pressure (0.82 g, 72%). M.p. (decomp.) = 90 °C (Found: C, 60.00; H, 5.40; N, 6.60. Calc. for $C_{22}H_{24}MnN_2O_4$: C, 60.69; H, 5.56; N, 6.43%).

Chlorobis[(4′*R*)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)phenolato-*N*,*O*]manganese(III) 13a. To a solution of $Mn(O_2CMe)_2{\cdot}4H_2O$ (0.64 g, 2.61 mmol) in absolute ethanol (20 cm^3) was added a solution of HL^{OH} (1.00 g, 5.23 mmol) in 10 cm^3 of the same solvent. The solution was stirred at reflux temperature for 1 h, then cooled at room temperature and LiCl (0.17 g, 4.01 mmol) added. The solution was again warmed at reflux temperature for 30 min, then concentrated to *ca.* 5 cm^3 and hexane added. A green-grey solid separated, which was recrystallized from dichloromethane and hexane (0.61 g, 50%). M.p. (decomp.) = 98 °C (Found: C, 56.0; H, 5.05; N, 5.85. Calc. for $C_{22}H_{24}ClMnN_2O_4$: C, 56.12; H, 5.14; N, 5.95%).

Dichloro[(4′*R*)-1-(diphenylphosphanyloxy)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)benzene-*N*,*P*]palladium(II) 1b. To a solution of L^{OP} (0.40 g, 1.07 mmol) in toluene (10 cm^3) at −78 °C was added a solution of $[PdCl_2(cod)]$[29] (cod = cycloocta-1,5-diene) (0.30 g, 1.07 mmol) in chloroform (10 cm^3). The mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure, affording an orange solid which was washed with diethyl ether (4 × 10 cm^3). The solid was recrystallized from dichloromethane and hexane (0.48 g, 81%). M.p. (decomp.) = 155 °C (Found: C, 50.02; H, 4.10; N, 2.45. Calc. for $C_{23}H_{22}Cl_2NO_2PPd$: C, 49.98; H, 4.01; N, 2.53%). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 135.0.

Chloro[(4′*R*)-1-(diphenylphosphanyloxy)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)benzene-*N*,*P*]methylpalladium(II) 2b. To a solution of L^{OP} (0.40 g, 1.07 mmol) in toluene (10 cm^3) at −78 °C was added a solution of [PdCl(Me)(cod)][30] (0.28 g, 1.07 mmol) in 10 cm^3 of the same solvent. After stirring for 3 h at room temperature the mixture was filtered through Celite under nitrogen. The solution was then concentrated to *ca.* 10 cm^3 under reduced pressure and hexane was added. Pale yellow crystals (0.45 g, 79%) separated after keeping the solution in a freezer overnight. M.p. (decomp.) = 115 °C (Found: C, 54.65; H, 4.87; N, 2.75. Calc. for $C_{24}H_{25}ClNO_2PPd$: C, 54.15; H, 4.73; N, 2.63%). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 149.4.

Acetonitrile-[(4′*R*)-1-(diphenylphosphanyloxy)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)benzene-*N*,*P*]methylpalladium(II) tetrafluoroborate 3b. To a solution of compound **2b** (0.30 g, 0.56 mmol) in dichloromethane (10 cm^3) was added a solution of silver tetrafluoroborate (0.11 g, 0.56 mmol) in 5 cm^3 of the same solvent in the dark. The solution was stirred for 20 min then acetonitrile (0.03 g, 0.73 mmol) was added. After stirring for 1 h the mixture was filtered through Celite under nitrogen and the filtrate concentrated to *ca.* 5 cm^3 and toluene added. An orange solid (0.20 g, 57%) separated after keeping the solution in a freezer for 3 d. M.p. (decomp.) = 112 °C (Found: C, 49.75; H, 4.35; N, 4.70. Calc. for $C_{26}H_{28}BF_4N_2O_2PPd$: C, 50.00; H, 4.52; N, 4.48%). Λ_M = 135 S cm^2 mol^{-1} (acetonitrile, 8.8×10^{-4} M). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 135.0.

[(4′*R*)-1-(Diphenylphosphanyloxy)-2-(4′-ethyl-3′,4′-dihydrooxazol-2′-yl)benzene-*N*,*P*](η^3-2-methylallyl)palladium(II) tetrafluoroborate 4b. To a solution of (cycloocta-1,5-diene)(η^3-2-methylallyl)palladium tetrafluoroborate[31] (0.30 g, 0.84 mmol) in dichloromethane (10 cm^3) was added a solution of L^{OP} (0.32 g, 0.84 mmol) in 10 cm^3 of the same solvent. After stirring for 1 h at room temperature, the mixture was concentrated under reduced pressure and dichloromethane (10 cm^3) and diethyl ether (10 cm^3) were added. An orange solid (0.40 g, 77%) separated after keeping the solution in a freezer overnight. M.p. (decomp.) = 130 °C (Found: C, 51.90; H, 4.35; N, 2.15. Calc. for $C_{27}H_{29}BF_4NO_2PPd$: C, 52.04; H, 4.69; N, 2.25%). Λ_M = 136 S cm^2 mol^{-1} (acetonitrile, 8.8×10^{-4} M). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 125.0.

Catalytic epoxidation reactions

All reactions were carried out under nitrogen at room temperature in a Schlenk tube (25 cm^3) equipped with a stirring bar and an air-tight rubber septum. Styrene (5.7 mmol) and octylbenzene (2.2 mmol) in dichloromethane (5 cm^3) were added to metal catalyst (0.044 mmol) and aliquat 336 (0.1 mmol). The GC analyses were performed by withdrawing several aliquots

with the aid of a hypodermic syringe. After the initial analysis, NaOCl (7 cm^3) was immediately added. The products (styrene oxide and phenylacetaldehyde) were quantified by the internal standard method. Oxidation products were isolated by column chromatography. Unchanged styrene was eluted with pentane and oxidation products were eluted with pentane–ether (75:25). The ^1H NMR spectrum indicated that the styrene oxide to phenylacetaldehyde ratio was 15:1. The enantiomeric excess of the epoxide was determined by capillary GC using a 30 m Carbowax column coupled to a 50 m Cyclodex-β column (oven temperature 85 °C isothermal). The optical purity of the epoxide was also analyzed by reduction to 1- and 2-phenylethanol by lithium aluminium hydride in thf and GC analysis on a 25 m Cyclodex-β column (oven temperature 85 °C isothermal).

Crystallography

The crystal data and data-collection parameters are given in Table 4. Crystals of complex **1a** were obtained by slow diffusion of hexane over a dichloromethane solution of the complex. Similarly, crystals of **2a** were obtained by slow diffusion of hexane over a toluene solution of the complex.

The crystal data for complex **1a** were measured on an Enraf-Nonius CAD4 four-circle diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($12 < \theta < 21°$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo-Kα radiation (λ 0.710 69 Å), using the ω–2θ scan technique. 6604 Reflections were measured in the range $2.21 < \theta < 29.96°$, 6257 of which were non-equivalent by symmetry [R_{int} (on I) = 0.012]. 5568 Reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls; significant intensity decay was not observed. Lorentz-polarization but not absorption corrections were made.

The structure was solved by Patterson synthesis, using the SHELXS computer program[32] and refined by full-matrix least squares with SHELXL 93,[33] using 6257 reflections (very negative intensities were ignored). The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0634P)^2]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f' and f'' were taken from ref. 34. The extinction coefficient was 0.0060(6). The chirality was defined from the Flack coefficient, 0.02(3).[35] Twenty-three H atoms were located by a difference synthesis and refined with an overall isotropic thermal parameter and 25 were computed and refined with an overall isotropic thermal parameter using a riding model. The final R (on F) factor was 0.032, wR (on $|F|^2$) = 0.085 and goodness of fit = 1.151 for all observed reflections. Number of refined parameters 617. Maximum shift/e.s.d. = 0.01, mean shift/e.s.d. = 0.00. Maximum and minimum peaks in the final difference synthesis were 1.056 and −0.482 e $Å^{-3}$, respectively.

The crystal data for complex **2a** were measured on a Philips PW-1100 four-circle diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($8 < \theta < 12°$) and refined by the least-squares method. Intensities were collected as above. 5254 Reflections were measured in the range $2.25 < \theta < 29.95°$, 4310 reflections being assumed as observed applying the condition $I > 2\sigma(I)$. Significant intensity decay was not observed. Corrections as above.

The structure was solved and refined as for complex **1a**, using 5204 reflections (very negative intensities were not considered). The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0368P)^2 + 1.5024P]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. The extinction coefficient was 0.006 55. The Flack coefficient was 0.05(3). A toluene group was located in a disordered position and the occupancy factor was refined for each position, giving 0.70(1) for the non-primed atoms. Nineteen H atoms were located from a difference synthesis and eight were computed and refined with an overall isotropic thermal parameter using a riding model for computed hydrogen atoms. The final R factor was 0.036, $wR = 0.074$ and goodness of fit = 0.987 for all observed reflections. Number of refined parameters 465. Maximum shift/e.s.d. = 4.0, mean = 0.15. Maximum and minimum peaks in final difference synthesis 0.448 and −0.340 e $Å^{-3}$, respectively.

CCDC reference number 186/662.

Table 1 Proton (250) and ^{13}C (50 MHz) NMR data[a] for the oxazoline ligands. Multiplicity[b] and coupling constants (in Hz) in parentheses

Ligand	δ(^1H)	δ(^{13}C)
HL^{OH}	1: 0.99 (3 H, t, 7.5)	1: 10.0
	2, 2′: 1.61 (1 H, ph, 7.0), 1.66 (1 H, ph, 7.0)	2: 28.7
	3: 4.25 (1 H, m)	3: 66.7
		4: 71.4
		5: 164.9
		6: 125.2
		7: 159.8
	4, 4′: 3.99 (1 H, pt, 7.8), 4.42 (1 H, dd, 9.5, 8.5)	Aromatic CH: 116.6, 118.5,
	8, 11: 7.00 (1 H, dd, 8.0, 1.0), 7.63 (1 H, dd, 8.0, 2.0)	127.9, 133.1
	9, 10: 6.84 (1 H, td, 7.5, 1.5), 7.34 (1 H, td, 7.5, 2.0)	
	OH: 12.3 (1 H, br)	
L^{OP}[c]	1: 0.95 (3 H, t, 7.5)	1: 9.6
	2, 2′: 1.56 (1 H, ph, 7.0), 1.68 (1 H, ph, 7.0)	2: 28.3
	3: 4.16 (1 H, m)	3: 66.3
		4: 71.0
		5: 164.6
		6: 110.3
		7: 159.6
	4, 4′: 3.86 (1 H, pt, 8.0), 4.30 (1 H, dd, 10.0, 8.0)	Aromatic CH: 133–117
	Aromatic H: 8.2–7.0 (14 H, m)	

[a] Spectra recorded in $CDCl_3$; ^{13}C NMR spectra were proton decoupled; δ in ppm. [b] Abbreviations: br = broad; d = doublet; h = hextuplet; m = multiplet; p = pseudo; t = triplet. [c] ^{31}P (101 MHz) NMR spectrum recorded in $CDCl_3$; proton decoupled; δ(^{31}P) 111.3.

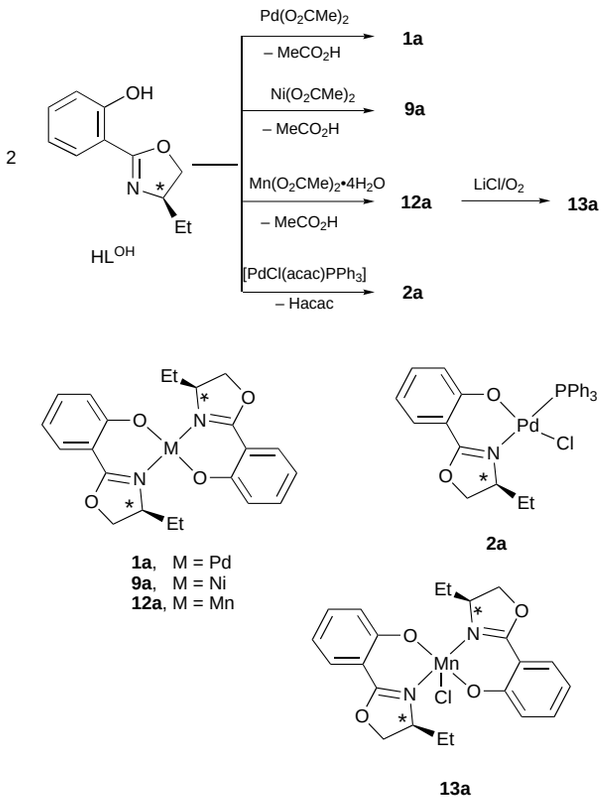
Results and Discussion

Ligands

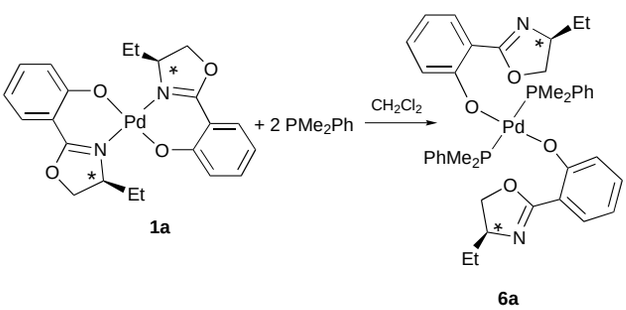
The oxazoline HL^{OH} was prepared in a one-pot synthesis from commercially available starting materials, following general published procedures with minor modifications. It was purified in two steps: first by a distillation under reduced pressure, followed by a silica gel column chromatography of the residue. The phosphinite L^{OP} was prepared from HL^{OH} by treatment with PPh_2Cl in presence of triethylamine. The ease with which the compound was oxidized is noteworthy and as a result it was not possible to measure the optical rotation of the pure compound accurately. Full details of the syntheses are given in the Experimental section; NMR data are given in Table 1. All methylene protons are diastereotopic appearing in different positions.

Complexes of L^{OH}

The proton of the hydroxo group in the oxazoline HL^{OH} was acid enough to react easily with metallic salts containing basic anions such as acetate or acetylacetonate (Scheme 1), affording compounds with the anionic bidentate chiral ligand. In this way we obtained homochiral bis(oxazolinato)-palladium, -nickel and -manganese complexes **1a**, **9a** and **12a** respectively, and $[PdCl L^{OH}(PPh_3)]$ **2a**. The chlorobis(oxazolinato)manganese(III) complex **13a** was obtained by refluxing ethanolic solutions of **12a** with LiCl under aerobic conditions. The reaction was monitored by EPR spectroscopy at room temperature. Initially, the ethanolic reaction mixture showed bands expected for manganese(II) compounds; the reflux was maintained until no absorption bands were observed in the EPR spectra, since the manganese(III) species are EPR silent.



Scheme 1



Scheme 2

The new complexes prepared in this work have been fully characterized by a range of techniques. Proton NMR data for the diamagnetic compounds of nickel and palladium are given in Tables 2 and 3. For the paramagnetic ones, magnetic susceptibility and EPR measurements have been done. In order to elucidate the isomeric composition in solution of **1a** and **9a**, ^{1}H NMR spectra were recorded in $CDCl_3$ over the range −50 to +50 °C. For **1a** the ^{1}H NMR study showed that, in solution, only one isomer was present. Moreover, the reactivity of **1a** towards dimethylphenylphosphine (Scheme 2) afforded a yellow solid **6a**; its ^{31}P NMR spectrum (over the range −50 to +50 °C) showed a single resonance (δ 33.8, at 298 K). Owing to the lack of a symmetry plane in the square-planar co-ordination sphere, the ^{1}H NMR spectrum showed two singlets for the different phosphine methyl groups. Besides, **1a** was characterized by X-ray diffraction, demonstrating that this isomer was the *trans* one. A similar *trans* structure has been determined by Nicholas and co-workers.[14] For **9a** the spectra of the green solution showed the presence of two isomers (*cis* and *trans*), with a major : minor isomer ratio of 2 : 1. The isomeric composition was unchanged in the whole range of temperature tested, and no line broadening was detected. So, the exchange between both isomers was not appreciable. Probably, the major isomer is the *trans* one, according to the analogous chemical shifts observed for the protons 2, 2′ and 3 for the palladium

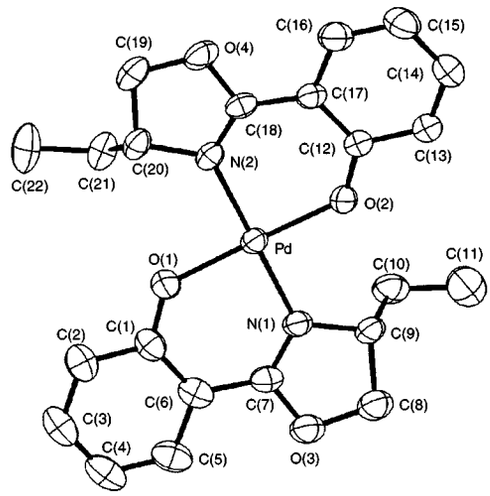


Fig. 1 View of the molecular structure of complex **1a** (molecule A), showing the atom labelling scheme. Hydrogen atoms have been omitted for clarity

compound **1a**. Similar nickel complexes described in the literature showed only one isomer in solution.[14]

The molecular structure of complex **1a** is shown in Fig. 1. Selected bond lengths and angles are presented in Table 5. The palladium atom is bonded to two nitrogen and two oxygen atoms; both pairs are in *trans* position (O–Pd–N angles 88.5–91.5 °C). This arrangement forces the molecule to orient the two ethyl groups of the oxazoline ligands to the same side of the molecular plane. The unit cell of **1a** contains two non-symmetric equivalent molecules which are pseudo-related by a two-fold axis parallel to the crystallographic *a* axis (Fig. 2). Each molecule is formed by six rings: this means two phenyl groups, two oxazoline groups and two six-membered rings; the latter are connected by the metal atom. Except for the phenyl groups, the other rings are not strictly planar. For the oxazoline moieties, the two sp^3-carbon atoms are twisted with regard to the heteroatoms and the sp^2-carbon atom of the ring. Moreover, the two six-membered rings containing the palladium are not coplanar. The angle between them is 7.82° for molecule A and 9.84° for B. On the other hand, the angle between the phenyl ring and the six-membered palladacycle is very small (0.2–3.7°). So, the loss of the planarity of the whole molecule is due to the tetrahedral distortion in the palladium co-ordination sphere. If we compare the two inequivalent molecules in the unit cell the shortest intermolecular distance, *i.e.* that between the palladium atom of one molecule and that of the other, is the Pd–N distance [*e.g.* Pd(A)···N(1B) 3.795, Pd(B)···N(2A) 3.687 Å].

The crystal structure of complex **2a** (Fig. 3) showed the presence of discrete mononuclear molecules, separated by van der Waals distances. Selected bond lengths and angles are listed in Table 6; all the bond distances are in the expected range. The complex exhibits an almost square-planar geometry with the nitrogen and phosphorus atoms in *trans* position. The following small displacements (Å) are observed from the least-squares plane defined by the atoms of the co-ordination sphere PdP-ClNO(1) (plane A): Pd, 0.022; P, 0.006; Cl, −0.016; N, 0.006; O(1), −0.018 Å. Slight alternative displacements from the least-squares plane NO(2)C(7)C(8)C(9) (plane B) are observed for the atoms of the oxazoline group: N, −0.071; O(2), 0.075; C(7), −0.001; C(8), −0.111; C(9), 0.108 Å. The cycle PdO(1)C(1)-C(6)C(7)N (plane C) shows a boat conformation with deviations of Pd −0.258 and C(6) −0.021 Å from the plane defined by the other four atoms. The angles between normal to the planes AB, AC and BC are 11.54, 14.71 and 4.43°, showing the planarity of the whole molecule. The greater *trans* influence of the PPh_3 ligand in the complex is clearly observed: the bond

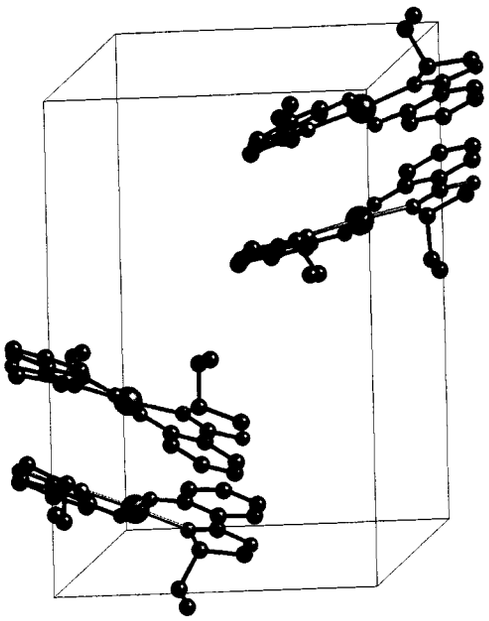


Fig. 2 Unit cell for complex **1a** showing the two non-symmetric equivalent molecules

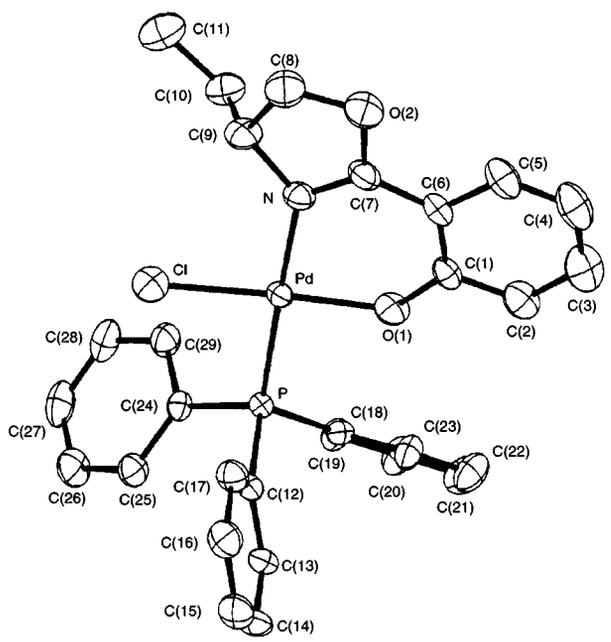
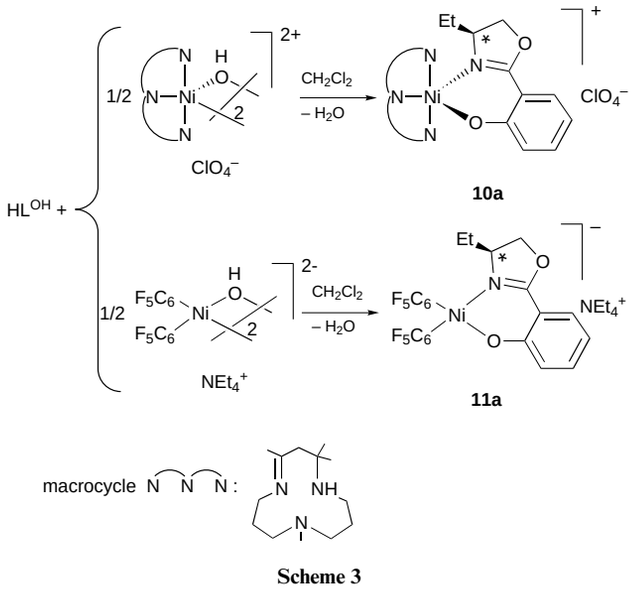


Fig. 3 View of the molecular structure of complex **2a**, showing the atom labelling scheme

distance Pd–N is 2.051(4) Å, whereas those in **1a** are in the range 1.999(4)–2.010(4) Å.

A powder sample of the paramagnetic bright green manganese(II) complex **12a** showed a $\mu_{eff} = 6.43\ \mu_B$ at 290 K, which was higher than expected for five unpaired electrons ($\mu_{eff} = 5.92\ \mu_B$ spin only) and the EPR spectrum (SUP 57274) showed an intense broad absorption in the $g \approx 2$ region at room temperature and at 77 K. However, for an ethanolic sample at 77 K, the six-line splitting by the ^{55}Mn nuclei ($I = \frac{5}{2}$) was observed.[36] The grey-green manganese(III) complex **13a** gave a $\mu_{eff} = 4.91\ \mu_B$ at 294 K close to the spin-only value expected for a d^4 ion (4.90 μ_B).[37]

Since OH bridges react easily towards protic acids,[28] we also studied the reactivity of HL^{OH} with bridging hydroxonickel species (Scheme 3), like $[\{NiL(\mu\text{-}OH)\}_2][ClO_4]_2$ (L = 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene) and $[NEt_4]_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]$ affording the paramagnetic $[NiL^{OH}(L)]ClO_4$ complex **10a** and the diamagnetic $[NEt_4][Ni(C_6F_5)_2L^{OH}]$ complex **11a**, respectively. In both cases, the L^{OH} ligand remained co-



Scheme 3

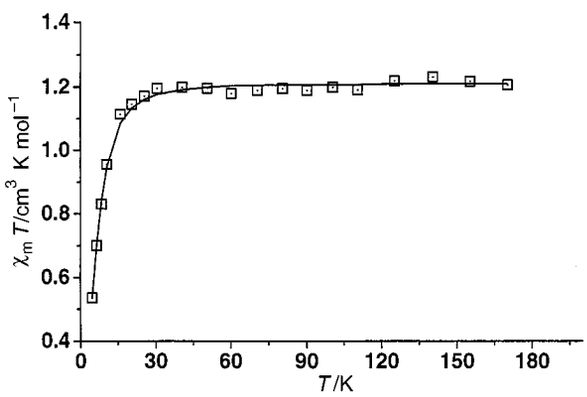


Fig. 4 Plot of $\chi_m T$ *vs.* T for complex **10a**. The solid line shows the best fitting (see Results and Discussion section)

ordinated in a bidentate form. For the five-co-ordinated complex **10a**, the magnetic susceptibility value at room temperature corresponds to two unpaired electrons ($\mu_{eff} = 3.22\ \mu_B$), but with a large orbital contribution. The molar magnetic susceptibility was measured over the temperature range 291–4.8 K. At room temperature $\chi_m T$ is 1.30 $cm^3\ K\ mol^{-1}$; this value decreases slowly until 25 K (1.17 $cm^3\ K\ mol^{-1}$) and at temperatures below 16 K the decrease is rapid, reaching 0.11 $cm^3\ K\ mol^{-1}$ at 4.8 K. The experimental data were fitted using equation (1) where x is D/kT (Fig. 4). The best fit is given by $D = 14.9\ cm^{-1}$ and $g = 2.20$. The parameter D is related to the geometry around the nickel(II) ion. In this case, the high value obtained is in accordance with the high anisotropy for the five-co-ordinated species.[38]

$$\chi_m = \frac{2Ng^2\mu^2}{3kT}\ \frac{2x^{-1} - 2\exp(-x)x^{-1} + \exp(-x)}{1 + 2\exp(-x)} \qquad (1)$$

The ^{19}F NMR spectrum of complex **11a** showed the signals of two different C_6F_5 groups according to the *cis* configuration. Moreover, in the proton NMR spectrum a large unexpected high-field shift for proton 3 with respect to that of complex **9a** was observed, probably due to the increase in electron density in the co-ordination sphere of the anionic complex.

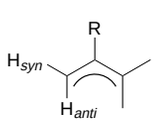
The reactivity of HL^{OH} with bridged hydroxopalladium species, $[\{PdPh(PPh_3)(\mu\text{-}OH)\}_2]$[25] was tested, but it was not possible to separate the expected organometallic compound, because the reaction mixture decomposed affording Pd^0. However, when the reaction was performed with bridging acetato species we obtained the $[Pd(C,N)L^{OH}]$ complexes, where C,N is a strongly anchored imine fragment [C,N is $C_6H_4CH{=}NCH_2Ph$

Table 2 Proton NMR (500 MHz) data[a] for the oxazolinato and phosphinite complexes. Multiplicity and coupling constants (in Hz) in parentheses

	Proton								
Complex	1	2, 2′	3	4, 4′	11	10	9	8	Other
1a	1.00 (t, 7.5)	1.70 (m), 2.08 (m)	4.48 (m)	4.43 (dd, 7.8, 3.25), 4.53 (t, 7.5)	7.57 (dd, 1.8, 8.5)	6.54 (ddd, 8.5, 7.0, 1.5)	7.20 (ddd, 8.5, 7.0, 1.5)	6.80 (dd, 1.0, 8.5)	—
2a	0.94 (t, 7.5)	1.66 (m), 2.08 (m)	4.80 (m)	4.37 (dd, 8.8, 3.75), 4.46 (t, 8.5)	7.56 (dd, 8.25, 1.8)	6.49 (ddd, 8.0, 7.0, 1.5)	7.02 (ddd, 8.5, 7.0, 1.5)	6.08 (dd, 8.5, 10)	—
3a	0.91 (t, 7.5)	1.70 (m), 1.92 (m)	4.77 (m)	4.34 (dd, 8.0, 4.5), 4.57 (t, 8.7)	7.55 (dd, 8.0, 2.0)	6.44	7.19	6.44	CH=N: 7.87 (s) CH_2N: 4.92 (d, 14), 5.19 (d, 14)
4a	0.58 (t, 7.5)	2.02 (m), 2.55 (m)	4.41 (m)	4.65 (dd, 8.0, 4.5), 3.99 (t, 8.5)	7.54 (dd, 8.0, 1.7)			6.51 (t, 7.9)	CH=N: 7.85 (s), 7.0–7.5 (m) OMe: 3.85 (s), 4.09 (s), 4.20 (s)
5a	0.93 (t, 7.7)	1.65 (m), 2.05 (m)	4.79 (m)	4.35 (dd, 8.7, 3.7), 4.44 (t, 8.5)	7.57 (dd, 8.0, 2)	6.50 (ddd, 8.0, 7.0, 1.5)	7.02 (ddd, 8.5, 7.0, 1.5)	6.00 (dd, 8.5, 1.0)	PPh_3: 7.4–7.5 (m), 7.7–7.8 (m) Mesityl: 2.14 (s), 2.27 (s), 2.80 (s), 6.38 (s), 6.52 (s)
6a	0.87 (t, 7.4)	1.13 (m), 2.05 (m)	4.16 (m)	3.90 (t, 7.7), 4.34 (t, 8.7)	7.50 (dd, 7.0, 1.5)	6.87 (d, 8.3)	6.73 (t, 6.5)	6.39 (t, 8.0)	PMe_2Ph: 1.58 (s), 1.64 (s), 7.6 (m)
9a[b]	0.97 (t, 7.5)	1.60 (m), 2.00 (m)	4.03 (m)	4.28 (m), 4.40 (m)	7.43 (m)	6.44 (m)	7.05 (m)	6.52 (m)	—
	1.02 (*t*, *7.5*)	*1.67* (*m*), *2.07* (*m*)	*3.95* (*m*)	*4.26* (*m*), *4.35* (*m*)					
11a	0.54 (t, 7.2)	1.60 (m) *c*	2.85 (m)	4.04 (dd, 8.5, 3.5), 4.07 (t, 8.5)	7.46 (dd, 7.8, 1.8)	6.32 (pt, 7.4)	7.01 (ddd, 8.6, 6.8, 1.8)	6.43 (pd, 8.4)	NEt_4: CH_3, 1.20 (t, 7.2); CH_2, 3.11 (q, 7.2)
1b[d]	1.03 (t, 7.5)	1.60 (m)	4.30 (m)	4.00 (dd, 8.5, 6.0), 4.40 (dd, 9.0, 9.8)	*e*	*e*	*e*	6.10 (m)	—
2b	0.69 (t, 7.5)	1.55 (m), 1.73 (m)	5.23 (m)	4.19 (dd, 8.7, 6.25), 4.54 (dd, 8.8, 9.8)	*e*	*e*	*e*	6.03 (dt, 7.5, 1.5)	Pd–Me: 0.58 (d, 3.5)[f]

[a] Spectra recorded in $CDCl_3$; δ in ppm, qnt = quintuplet. [b] In italic, data for the minor isomer. No assignment was possible for the aromatic protons of the two isomers. [c] Overlapped with the resonance of the methyl proton of the tetraethylammonium cation. [d] Spectrum recorded on a 300 MHz spectrometer. [e] Aromatic protons in the range δ 8.2–6.5. [f] ^1H-{^{31}P} NMR spectrum has been recorded.

Table 3 Selected ^1H NMR (500 MHz) data[a] for complexes **7a** and **8a**. Coupling constants (in Hz) in parentheses



	1[b]		2, 2′		3		4, 4′[c]		H_{syn}[d]		H_{anti}		R	
Complex														
7a	0.91 (7.5)	0.89 (7.5)	1.54 (m) 1.63 (m)	1.72 (m) 1.79 (m)	4.10 (m)	4.16 (m)	4.24 (8.5, 1.5) 4.39 (15, 8.5)	4.25 (8.5, 1.5) 4.39 (17.5, 6.5)	3.12 (3.0) 3.77 (3.0)	3.22 (2.5) 3.78 (2.5)	2.53 2.95	2.52 2.90	2.11	2.16
8a	1.18 (7.5)	0.98 (7.5)	1.80 (m) 1.70 (m)	1.55 (m) 1.90 (m)	3.80 (m)	4.45 (m)	3.16 (8.5, 1.5) 3.43 (15, 8.5)	4.41 (8.5, 1.5) 4.51 (15, 8.5)	3.16 (pt) 3.52 (br)	3.22 (br) 3.48 (br)	2.40 2.80	2.33 2.90	5.30 (m)	5.20 (m)

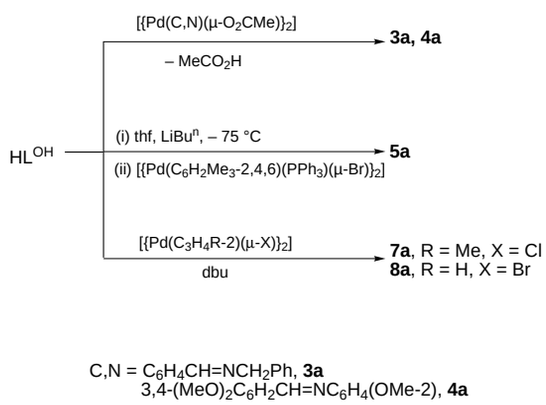
[a] Spectra recorded in $CDCl_3$; δ in ppm. Left column, major isomer; right column, minor isomer. [b] Triplet. [c] Doublet of doublets. [d] Doublet.

for **3a** and 3,4-$(MeO)_2C_6H_2CH{=}NC_6H_4$(OMe-2) for **4a**] (Scheme 4). Also, the reactivity of HL^{OH} with bridging bromo precursors in the presence of a base, such as dbu or $LiBu^n$, was studied. In the latter case the oxazoline HL^{OH} was previously deprotonated by $LiBu^n$ in thf and the resulting lithium salt added directly over the bridging bromo precursor, [{Pd-($C_6H_2Me_3$-2,4,6)(PPh_3)(μ-Br)}$_2$], giving the aryl complex **5a**. The geometry of the complex must be analogous to that observed in **2a** since the proton NMR spectra of the ligands are identical. The lack of a symmetry plane in the co-ordination sphere was evident because the two *o*-methyl and the two phenyl protons of the mesitylene ligand appeared with different chemical shifts. Using dbu as a base, it was possible to separate the allyl complexes **7a** and **8a** in good yields (Scheme 4). These were obtained as a mixture of two isomers (ratio 55:45), due to the position of the ethyl group of the oxazoline ligand relative to the substitution on the central allyl carbon (*exo* and *endo* isomers).[13] A variable-temperature ^1H NMR study of complex **7a** showed that the isomer ratio did not suffer significant changes over the temperature range −50 to +50 °C. Furthermore, a change was not observed in the isomer composition after standing the complex at room temperature in $CDCl_3$ for a week. Therefore the isomer interconversion is not appreciable (Scheme 5). Besides, the averaging of the *syn* and *anti* protons of the allyl fragment was not observed.

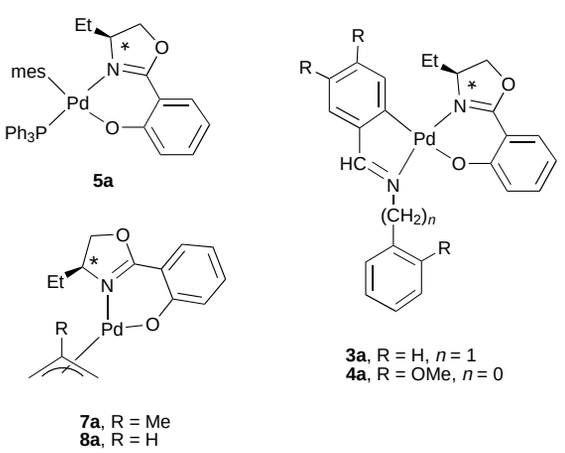
Nicholas and co-workers[13] have reported a crystal structure determination of an allyl complex, containing this type of L^{OH} ligand. Low-temperature NMR spectra showed only one isomer in solution, but at room temperature two diastereoisomers, *exo* and *endo*, were observed in a 1:1 ratio.

Table 4 Crystal data for complexes **1a** and **2a**

	1a	**2a**
Formula	$C_{22}H_{24}N_2O_4Pd$	$C_{29}H_{27}ClNO_2PPd\cdot C_7H_8$
M	486.84	686.50
Crystal dimensions/mm	0.1 × 0.1 × 0.2	0.1 × 0.2 × 0.1
T/K	293	293
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$
a/Å	11.094(3)	20.420(3)
b/Å	17.301(11)	18.078(3)
c/Å	11.3899(12)	8.803(2)
β/°	106.87(2)	
U/Å^3	2092(2)	3250(2)
Z	4	4
D_c/g cm^{-3}	1.564	1.401
F(000)	992	1404
μ/mm^{-1}	0.917	0.735
Total no. reflections measured	6604	5254
No. reflections used [$I > 2\sigma(I)$]	6257	4310
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0329, 0.0850	0.0361, 0.0742
(all data)	0.0434, 0.0982	0.0706, 0.1964
Goodness of fit	1.151	0.987



C,N = $C_6H_4CH{=}NCH_2Ph$, **3a**
$3,4\text{-}(MeO)_2C_6H_2CH{=}NC_6H_4(OMe\text{-}2)$, **4a**



Scheme 4 mes = $C_6H_2Me_3$-2,4,6

Complexes of L^{OP}

Six-membered metallic rings, containing four sp^2 atoms, were obtained, with the bidentate anionic moiety N,O*. In particular, the allyl complexes in solution were rigid on the NMR timescale. However, similar complexes with N,O*,[13] N,P*[12] or N,N*[39] ligands showed non-rigid behaviour. In some cases, it has been stated that the ligand itself maintains a rigid conformation.[40] In other situations, a twist in the six-membered ring contributes to the non-rigidity of the complex.[39]

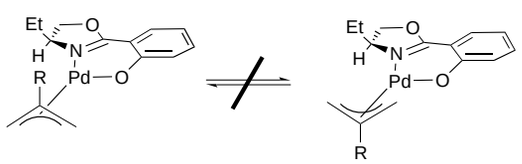
We have obtained complexes with an N,P* neutral ligand containing a seven-membered ring and with allyl or methyl groups.

Table 5 Selected bond lengths (Å) and angles (°) for complex **1a**

Pd(A)–O(1A)	1.968(3)	Pd(B)–O(1B)	1.967(4)
Pd(A)–O(2A)	1.979(3)	Pd(B)–O(2B)	1.977(4)
Pd(A)–N(1A)	2.001(4)	Pd(B)–N(1B)	1.999(4)
Pd(A)–N(2A)	2.010(4)	Pd(B)–N(2B)	2.004(4)
N(1A)–C(7A)	1.306(7)	N(1B)–C(7B)	1.282(7)
N(2A)–C(18A)	1.286(7)	N(2B)–C(18B)	1.288(7)
O(1A)–C(1A)	1.320(7)	O(1B)–C(1B)	1.310(6)
O(2A)–C(12A)	1.300(6)	O(2B)–C(12B)	1.308(6)
C(6A)–C(7A)	1.443(8)	C(6B)–C(7B)	1.443(8)
C(1A)–C(6A)	1.408(9)	C(1B)–C(6B)	1.427(7)
C(12A)–C(17A)	1.429(7)	C(12B)–C(17B)	1.416(8)
C(17A)–C(18A)	1.423(8)	C(17B)–C(18B)	1.414(9)
O(1A)–Pd(A)–O(2A)	176.7(2)	O(2B)–Pd(B)–O(1B)	177.1(2)
O(1A)–Pd(A)–N(1A)	91.5(2)	O(2B)–Pd(B)–N(1B)	88.5(2)
O(2A)–Pd(A)–N(1A)	88.5(2)	O(1B)–Pd(B)–N(1B)	91.5(2)
O(1A)–Pd(A)–N(2A)	88.8(2)	O(2B)–Pd(B)–N(2B)	90.8(2)
O(2A)–Pd(A)–N(2A)	91.4(2)	O(1B)–Pd(B)–N(2B)	89.4(2)
N(1A)–Pd(A)–N(2A)	176.6(2)	N(1B)–Pd(B)–N(2B)	177.0(2)

Table 6 Selected bond lengths (Å) and angles (°) for complex **2a**

Pd–O(1)	1.991(3)	N–C(7)	1.287(7)
Pd–N	2.051(4)	C(6)–C(7)	1.438(8)
Pd–P	2.2666(10)	C(1)–C(6)	1.422(7)
Pd–Cl	2.2873(12)	O(1)–C(1)	1.309(5)
O(1)–Pd–N	89.6(2)	O(1)–Pd–Cl	176.93(11)
O(1)–Pd–P	89.13(9)	N–Pd–Cl	92.61(12)
N–Pd–P	178.46(12)	P–Pd–Cl	88.63(4)



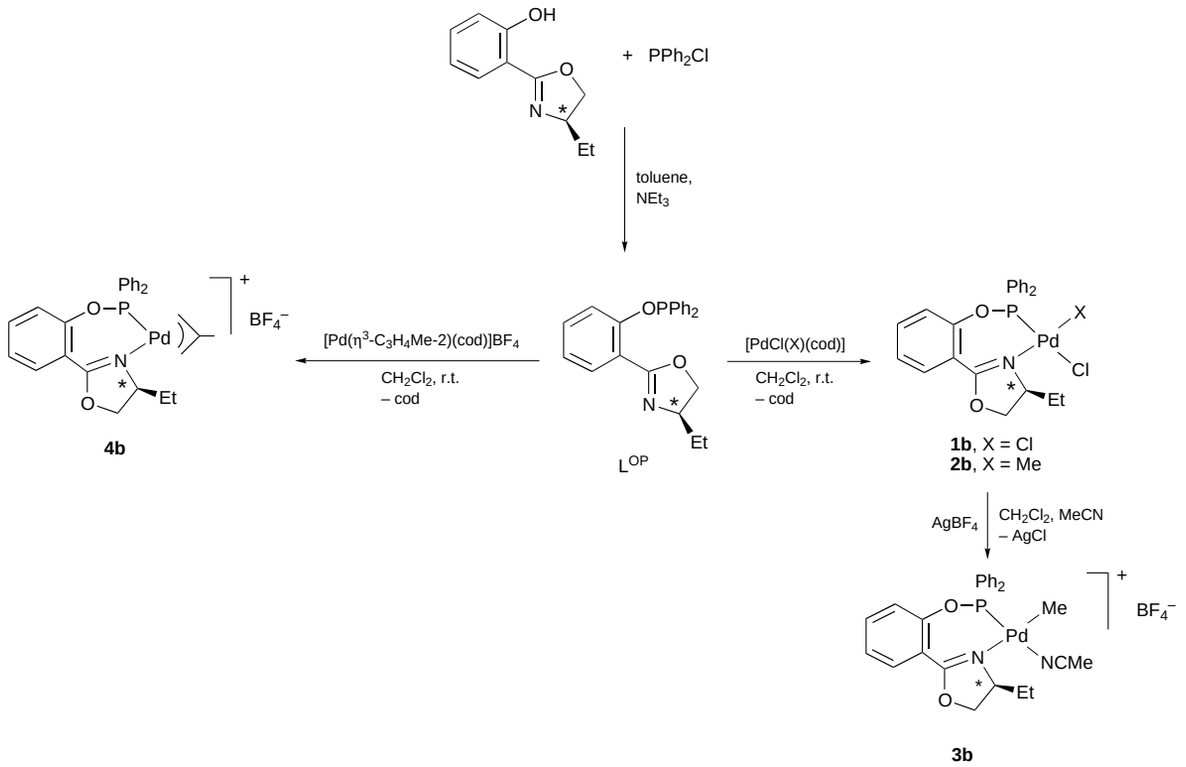
Scheme 5

The neutral (**1b** and **2b**) and cationic (**3b** and **4b**) palladium complexes were prepared by substitution reactions (Scheme 6). The neutral complexes gave very well defined ^{1}H NMR spectra at room temperature (Table 2). The resonance of the methyl bonded to the palladium atom for **2b** appeared as a doublet at δ 0.58 [^3J(PH) = 3.5 Hz]. The value of this coupling constant is as expected for a *cis* disposition between the methyl and the phosphorus atom.[41] However, the cationic complexes gave very broad NMR signals even at −70 °C. Since the neutral complexes are rigid and the substituents in the different ligands were the same as those used in the rigid N,O* ligand complexes, the dynamic behaviour in these complexes probably depends on the *trans* labilizing effect of the phosphorus atom, which would be enough to labilize MeCN or the allyl group. These results show the importance of the electronic factors in the activation processes in this type of asymmetric complexes.[42]

Similar Ph_2P-oxazoline allyl complexes prepared with the symmetric η^3-1,3-$Ph_2C_3H_3$ allyl group showed the presence, either in the solid state or in solution, of two diastereoisomers, *exo* and *endo*, depending on the relative position of the substituent on the chiral carbon with respect to the central C atom of the allyl moiety. In solution the two isomers occur nearly in the same proportion.[40]

Oxidation of styrene

Recently, chiral ruthenium pyridyloxazoline complexes have been reported to catalyse the asymmetric epoxidation of olefins using sodium periodate as the oxygen donor.[43] Similarly chiral ruthenium bis(2-pyridyloxazoline) complexes were used as cat-



Scheme 6 r.t. = Room temperature

Table 7 Results of styrene oxidation with NaOCl

Complex	Conversion (%)	*t*/h	Epoxide (%)[a]	Selectivity (%)[b]
1a	3	24	Traces	—
9a	4	24	Traces	—
13a	12	3	6	50[c]

[a] Based on starting styrene. [b] Epoxide yield/% conversion. [c] Side products detected: PhCHO (1%) and $PhCH_2CHO$ (1.2%).

alysts for epoxidations with iodosylbenzene[44] and RCHO/O_2.[45] These results prompted us to study the possibility of using chiral hydroxyphenyl oxazoline ligands for asymmetric alkene oxidations.

The activity of complexes **1a**, **9a** and **13a** was investigated under a standard set of conditions by using catalytic amounts of the corresponding complex together with styrene as the test olefin in a biphasic system. In the absence of the catalysts, the olefin was scarcely oxygenated by ClO^- alone under identical reaction conditions. We verified that the simple salt $Mn(O_2CMe)_2$ resulted in no epoxidation and styrene oxide was stable under the reaction conditions. Table 7 summarizes our trials on the catalytic epoxidation of styrene with NaOCl.

The nature of the metal has an important influence on the catalytic properties of the oxazoline complexes. It is also known that there exist very specific ligand requirements in order for nickel(II) species to participate in catalytic epoxidation with OCl^-. Nickel(II)–1,4,8,11-tetraazacyclotetradecane systems[46] are active but (5,10,15,20-tetraphenylporphyrinato)nickel(II) is completely inactive. Square-planar nickel complexes containing N_2O_2 co-ordination sites, *i.e.* [Ni(salen)][47] [H_2salen = *N*,*N*′-bis(salicylidene)ethane-1,2-diamine] or salen analogues such as [Ni(babp)][48] {H_2babp = *N*,*N*′-[6,6′-(2,2′-bipyridyl)]dibenzimidic acid} were reported to catalyse alkene oxidation using NaOCl under phase-transfer conditions, although the latter complex required much longer induction periods. The square-planar palladium and nickel complexes **1a** and **9a** were not effective under the experimental conditions.

Modest conversions and selectivities were observed with complex **13a**. For chiral salen-based manganese(III) catalysts the presence of bulky groups in the salen ligand is crucial to its stability and selectivity.[49] Bleaching of catalyst **13a** occurs a considerable time before the end of olefin conversion. The major product of styrene oxidation was styrene oxide but small amounts of benzaldehyde (1%) and phenylacetaldehyde (1.2%) were also detected by GC and NMR spectroscopy from the reaction mixtures. The epoxide was isolated and a fairly low enantioselectivity [3% enantiomeric excess of (*S*)-(−)-styrene oxide] was detected using a 30 m Carbowax and a 50 m Cyclodex-β column. This reaction was run several times and the results were reproducible. An additional analysis was performed to check the optical purity. The isolated epoxide was reduced to 1-phenylethanol by lithium aluminium hydride and was analyzed using a 25 m Cyclodex-β column. No enantioselectivity was detected within the error of the measurement by using racemic samples under the same conditions.

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