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Novel chiral 1,5-diaza-3,7-diphosphacyclooctane ligands and their transition metal complexes

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Reaction of bis(hydroxymethyl)phenylphosphine with (*R*)- or (*S*)-α-methylbenzylamine leads to the novel cyclic chiral bisphosphine ligands 1,5-(*R*,*R*)- and 1,5-(*S*,*S*)-bis(α-methylbenzyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane (**1r** or **1s**). Novel chiral chelate complexes of Pt^{II} (**2r**, **3r** and **3s**), Pd^{II} (**4s**, **5s**) and Re^{I} (**6r**) have been obtained by reaction of **1r** or **1s** with $[MCl_2(cod)]$ (M = Pt, Pd; cod = 1,5-cyclooctadiene) and $[\{ReBr(CO)_3(thf)\}_2]$. Compounds **1**–**6** were characterised by multinuclear NMR (^1H, ^{13}C, ^{31}P) and IR spectroscopy. The former technique revealed the presence of two inequivalent phosphorus atoms in **6r**. The molecular structure of **1r** confirmed the absolute configuration of the chiral centers and a chair-chair conformation of the heterocycle with equatorial orientation of the substituents on phosphorus and axial on nitrogen atoms. Compound **1s** was used to form a palladium catalyst for the co-polymerisation of carbon monoxide and norbornadiene. The structures of the co-polymers obtained were characterised by GPC, ^1H and ^{13}C NMR spectroscopy and elemental analysis.

Introduction

Design of chiral ligands has been a central subject in the development of catalytic and stoichiometric asymmetric reactions. As tertiary phosphines are highly efficient ligands in these reactions, syntheses of new chiral phosphines, especially chelating phosphines, have received considerable attention.[1–3]

Mannich-type reactions of various phosphines, formaldehyde and optically active amines were demonstrated to be a powerful method of constructing chiral, air-stable aminomethylphosphines, which are promising ligands for the design of enantioselective homogeneous catalysts.[4–6] The main route is the reaction of oxymethyldiphenylphosphines with chiral primary amines to give a number of chelate ligands with P–$CH_2N(R^*)CH_2$–P bisphosphine fragments. Starting from the work of Markl *et al.*[7,8] and Tzschach and co-workers[9,10] a wide variety of chelate complexes of this type has been obtained, including phosphines with cyclodextrin,[11] dendrimer,[12,13] amino acid and peptide[14] moieties. However changes in the steric and/or electronic properties of the ligands are known to dramatically influence the selectivity and the reactivity of transition metal complexes. We are interested in preparing new polydentate heterocyclic ligands and their transition metal complexes, especially chiral ones.[15–17] It has been shown that 1,5-diaza-3,7-diphosphacyclooctanes are air-stable crystalline ligands that form predominantly chelate complexes with transition metals. A distinguishing feature of these complexes is a chair-boat conformation of the metal-containing bicyclo-[3.3.1]nonane backbone with one nitrogen atom situated near the metal atom.[18–20] Attempts to prepare optically active 1,5-diaza-3,7-diphosphacyclooctanes from amino acids failed; instead, 1,3-diaza-5-phosphorinanes were formed.[21–23] Here we describe the novel cyclic chiral bisphosphine ligands 1,5-(*R*,*R*)- and 1,5-(*S*,*S*)-bis(α-methylbenzyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane (**1r** and **1s**) and novel chiral chelate complexes of Pt^{II} (**2r**, **3r** and **3s**), Pd^{II} (**4s**, **5s**) and Re^{I} (**6r**).

Experimental

General

All manipulations were carried out with standard high-vacuum and dry-nitrogen techniques. Norbornadiene was purchased from Aldrich, and CO was 99.5% pure. NMR spectra: Avance DRX 400 (Bruker), standards: ^1H NMR (400 MHz): C_6H_6, ^{13}C NMR (100.6 MHz): internal solvent, ^{31}P NMR (162 MHz): external 85% H_3PO_4; CXP-200 (Bruker): ^1H NMR (200 MHz), ^{13}C NMR (50.4 MHz). The IR spectra were recorded as KBr mulls on a Perkin-Elmer System 2000 FT-IR spectrometer in the range 350–4000 cm^{-1} and on an IFS-113v FT-IR spectrometer in the range 100–450 cm^{-1}. The melting points were determined in sealed capillaries and are uncorrected. Specific rotation was determined on a Perkin Elmer Model 341 Polarimeter at 589 nm.

Molecular weights and molecular weight distributions of co-polymers in tetrahydrofuran were measured relative to polystyrene standards by a Waters GPC instrument at 25 °C.

X-Ray crystallography

X-ray diffraction data were collected on a Siemens SMART CCD diffractometer (radiation: Mo-Kα, $\lambda = 0.71073$ Å; method: ω scans rotation). Absorption correction was performed using the program SADABS.[24] 1200 reflections were used for refinement of the unit cell. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically (SHELX97).[25] H atoms were refined isotropically. The phenyl protons were calculated on idealised positions. Crystal data, structure refinement for compound **1r**, selected bond lengths (Å) and angles (°) for the conformers **1r′** and **1r″** are given in Tables 1 and 2.

CCDC reference number 200855.

See http://www.rsc.org/suppdata/dt/b3/b300754e/ for crystallographic data in CIF or other electronic format.

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Table 1 Crystal data and structure refinement for compound **1r**

Formula	$C_{32}H_{36}N_2P_2$
Formula weight	510.57
Crystal system	Monoclinic
Space group	*C*2
Unit cell dimensions	
a/Å	23.052(12)
b/Å	5.472(3)
c/Å	22.567(12)
β/°	100.552(10)
V/nm^3	2.80(1)
Z	4
Temperature/K	223(2)
Wavelength/Å	0.71073
D_c/g cm^{-3}	1.212
Absorption coefficient/mm^{-1}	0.179
Crystal size/mm^3	0.20 × 0.10 × 0.05
θ Range for data collection/°	0.92–26.37
F(000)	1088
Index ranges, *hkl*	−21 to 28, −6 to 6, −28 to 27
Reflections collected	8210
Independent reflections (R_{int})	5349 (0.0678)
Completeness to θ = 26.37° (%)	99.4
Absorption correction	SADABS
Max., min. transmission	0.9911, 0.9652
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5349/1/367
Goodness-of-fit on F^2	1.018
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0718, $wR2$ = 0.1428
R indices (all data)	$R1$ = 0.1378, $wR2$ = 0.1758
Absolute structure parameter	−0.01(17)
Largest diff. peak, hole/e Å^{-3}	0.266, −0.240

Table 2 Selected bond lengths (Å) and angles (°) for conformers **1r′** and **1r″**

1r′		**1r″**	
P(1A)–C(1A)	1.887(7)	P(1B)–C(1B)	1.915(6)
P(1A)–C(2A)	1.906(6)	P(1B)–C(2B)	1.889(6)
P(1A)–C(3A)	1.819(6)	P(1B)–C(3B)	1.838(5)
N(1A)–C(2A′)	1.447(7)	N(1B)–C(2B′)	1.457(7)
N(1A)–C(1A)	1.450(7)	N(1B)–C(1B)	1.461(7)
N(1A)–C(9A)	1.467(8)	N(1B)–C(9B)	1.474(7)
C(3A)–P(1A)–C(1A)	101.4(3)	C(3B)–P(1B)–C(1B)	99.3(3)
C(3A)–P(1A)–C(2A)	97.2(3)	C(3B)–P(1B)–C(2B)	102.1(3)
C(1A)–P(1A)–C(2A)	100.6(3)	C(2B)–P(1B)–C(1B)	99.2(3)
C(2A′)–N(1A)–C(1A)	113.6(5)	C(2B′)–N(1B)–C(9B)	111.7(5)
C(2A′)–N(1A)–C(9A)	113.0(5)	C(2B′)–N(1B)–C(1B)	113.9(4)
C(1A)–N(1A)–C(9A)	115.7(5)	C(1B)–N(1B)–C(9B)	118.2(5)
N(1A)–C(1A)–P(1A)	116.9(5)	N(1B)–C(1B)–P(1B)	117.4(4)
N(1A′)–C(2A)–P(1A)	118.2(4)	N(1B′)–C(2B)–P(1B)	116.0(4)

Preparations

1,5-(*R*,*R*)-Bis(α-methylbenzyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane (1r). A solution of bis(hydroxymethyl)-phenylphosphine (2.69 g, 16 mmol) and (*R*)-α-methylbenzylamine (1.91 g, 16 mmol) in 40 mL of ethanol was refluxed for 6 h. White crystals were collected by filtration, washed with ethanol and dried under vacuum. Yield: 3.28 g, 80%; mp 170–172 °C. ^{1}H NMR ($CDCl_3$): δ 1.11 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH_3), 3.09 (br d, $^2J_{HH}$ = 14 Hz, 2H, $PCH^{1A}{}_2N$), 3.37 (br d, $^2J_{HH}$ = 14 Hz, 2H, $PCH^{1B}{}_2N$), 3.53 (br d, $^2J_{HH}$ = 14 Hz, 2H, $PCH^{2A}{}_2N$), 3.73 (br d, $^2J_{HH}$ = 14 Hz, 2H, $PCH^{2B}{}_2N$), 4.54 (br q, $^3J_{HH}$ = 6.4 Hz, 2H, C*H), 7.04–7.33 (m, 20H, C_6H_5). ^{13}C NMR (DMF-d_7): δ 20.67 (d, $^1J_{CH}$ = 126.5 Hz, CH_3), 57.35 (tt, $^1J_{CH}$ = 136.7 Hz, $^1J_{CP} \approx {}^3J_{CP} \approx 9$ Hz, C^1), 61.14 (dt, $^1J_{CH}$ = 130.3 Hz, $^3J_{CP} \approx 9$ Hz, C*), 61.41 (tt, $^1J_{CH}$ = 134.6 Hz, $^1J_{CP} \approx {}^3J_{CP} \approx 9$ Hz, C^2), 127.64 (d, $^1J_{CH}$ = 152.0 Hz, C^{10}), 128.36 (d, $^1J_{CH}$ = 157.7 Hz, C^6), 129.12 (m, $^1J_{CH} \approx 160$ Hz, $C^{5,8,9}$), 133.28 (dd, $^1J_{CH}$ = 160.2 Hz, $^3J_{CP}$ = 10.2 Hz, C^4), 141.19 (d, $^1J_{CP}$ = 7.6 Hz, C^3), 145.92 (s, C^7). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −64.4 (br s). α = +44 for **1r** (c = 0.21, $CHCl_3$). Anal. Calc. for $C_{32}H_{36}N_2P_2$ (M = 510): C, 75.29; H, 7.06; N, 5.49; P, 12.16. Found: C, 75.5; H, 7.0; N, 5.6; P, 12.6%.

Compound **1s** was prepared similarly to **1r** from (*S*)-α-methylbenzylamine. Yield: 75%; α = −44 for **1s** (c = 0.19, $CHCl_3$).

Bis[1,5-(*R*,*R*)-bis(α-methylbenzyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane]platinum(II) dichloride (3r). [$PtCl_2$-(cod)] (0.43 g, 1.2 mmol) in 20 mL of CH_2Cl_2 was added to a solution of **1r** (1.18 g, 2.3 mmol) in 10 mL of CH_2Cl_2. The next day the solvent was removed in vacuum, **3r** was crystallised from chloroform and white crystals were collected by filtration, washed with chloroform and dried under vacuum. Yield: 1.35 g, 91%, mp 192–194 °C. ^{1}H NMR ($CDCl_3$): δ 1.58 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3), 3.40–3.45 (br m, $^2J_{HH}$ = 13.2 Hz, 4H, $PCH^A{}_2N$), 4.03–4.06 (br m, $^2J_{HH}$ = 13.2 Hz, 4H, $PCH^B{}_2N$), 4.38 (br q, $^3J_{HH}$ = 6.8 Hz, 2H, C*H), 7.07–7.54 (m, 20H, C_6H_5). ^{13}C{^{1}H} NMR (DMF-d_7): δ 15.20 (br s, CH_3), 46.25 (br s, C^1), 51.72 (br s, C^2), 66.53 (t, $^3J_{CP}$ = 13.2 Hz, C*H), 128.21 (s, C^{10}), 128.98 (s, C^8), 129.21 (s, C^9), 129.47 (br s, C^5), 131.21 (br s, C^6), 131.30 (br s, C^4) 141.08 (s, C^7). C^3 was not observed. ^{31}P{^{1}H} NMR (CH_2Cl_2): δ −12.5 ($^1J_{PtP}$ = 2400 Hz); (DMF): δ −10.6 ($^1J_{PtP}$ = 2368 Hz). α = −35 for **3r** (c = 0.07, DMF). Anal. Calc. for $C_{64}H_{72}Cl_2N_4P_4Pt$ (M = 1286): C, 59.72; H, 5.60; N, 4.36; P, 9.64. Found: C, 60.1; H, 5.3; N, 4.6; P, 9.6%.

Complex **2r** was not obtained in the pure state, and was characterised only in the reaction mixture by ^{31}P NMR spectroscopy.

Complex **3s** was prepared similarly to **3r** from **1s**. Yield: 90%, α = +35 for **3s** (c = 0.07, DMF).

[1,5-(*S*,*S*)-Bis(α-methylbenzyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane]dichloropalladium(II) (4s). [$PdCl_2$(cod)] (0.17 g, 0.6 mmol) in 20 mL of CH_2Cl_2 was added to a solution of **1s** (0.30 g, 0.6 mmol) in 10 mL of CH_2Cl_2. The next day the solvent was removed in vacuum, **4s** was crystallised from chloroform and white crystals were collected by filtration, washed with chloroform and dried under vacuum. Yield: 0.2 g, 50%, mp 144–146 °C. ^{1}H NMR ($CDCl_3$): δ 1.56 (d, $^3J_{HH}$ = 7.2 Hz, 6H, CH_3), 3.28 (dd, $^2J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 6.7 Hz, 2H, $PCH^{1A}{}_2N$), 3.38 (dd, $^2J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 7.2 Hz, 2H, $PCH^{2A}{}_2N$), 3.77 (d, $^2J_{HH}$ = 13.8 Hz, 2H, $PCH^{1B}{}_2N$), 3.97 (d, $^2J_{HH}$ = 13.8 Hz, 2H, $PCH^{2B}{}_2N$), 4.78 (br s, 2H, C*H), 6.95–7.45 (m, 20H, C_6H_5). ^{13}C{^{1}H} NMR (DMF-d_7): δ 16.73 (s, CH_3), 46.72 (d, $^1J_{PC}$ = 33.6 Hz, C^1), 49.50 (d, $^1J_{PC}$ = 38.9 Hz, C^2), 63.74 (br s, C*H), 127.50 (s, C^{10}), 127.90 (d, $^3J_{PC}$ = 5.1 Hz, C^5), 128.02 (s, C^8), 128.39 (s, C^9), 130.48 (s, C^6), 132.04 (s, C^4) 141.74 (s, C^7). C^3 was not observed. ^{31}P{^{1}H} NMR (CH_2Cl_2–DMF): δ −6.9. α = +34 for **4s** (c = 0.03, CH_2Cl_2). Anal. Calc. for $C_{32}H_{36}Cl_2N_2P_2Pd$ (M = 687): C, 55.90; H, 5.24; N, 4.08; P, 9.03. Found: C, 55.7; H, 4.9; N, 4.2; P, 8.9%.

Bis[1,5-(*S*,*S*)-bis(α-methylbenzyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane]palladium(II) dichloride (5s). [$PdCl_2$(cod)] (0.14 g, 0.5 mmol) in 20 mL of CH_2Cl_2 was added to a solution of **1s** (0.54 g, 1.1 mmol) in 10 mL of CH_2Cl_2. The next day the solvent was removed in vacuum, **5s** was crystallised from chloroform, and white crystals were collected by filtration, washed with chloroform and dried under vacuum. Yield: 0.56 g, 88%, mp 157–159 °C. ^{1}H NMR (DMF-d_7): δ 1.58 (br s, 12H, CH_3), 3.27 (br d, $^2J_{HH}$ = 12 Hz, 8H, $PCH^A{}_2N$), 3.95 (br d, $^2J_{HH}$ = 12 Hz, 8H, $PCH^B{}_2N$), 4.39 (br q, $^3J_{HH}$ = 6 Hz, 4H, C*H), 7.11–7.52 (m, 40H, C_6H_5). ^{13}C NMR (DMF-d_7): δ = 15.31 (q, $^1J_{CH}$ = 126.0 Hz, CH_3), 47.21 (br t, $^1J_{CH}$ = 147.3 Hz, C^1), 50.99 (br t, $^1J_{CH}$ = 147.3 Hz, C^2), 66.58 (dt, $^1J_{CH}$ = 138.3 Hz, $^3J_{CP}$ = 5.3 Hz, C*H), 128.23 (d, $^1J_{CH}$ = 165.7 Hz, C^{10}), 129.01 (d, $^1J_{CH}$ = 159.2 Hz, C^8), 129.23 (d, $^1J_{CH}$ = 159.2 Hz, C^9), 129.50 (br d, $^1J_{CH}$ = 160.6 Hz, C^5), 131.04 (br d, $^1J_{CH}$ = 160.6 Hz, C^6), 131.30 (br d, $^1J_{CH}$ = 163.2 Hz, C^4) 141.03 (s, C^7). C^3 was not observed. ^{31}P{^{1}H} NMR (DMF): δ 0.3. α = +43 for **5s** (c = 0.02, DMF). Anal. Calc. for $C_{64}H_{72}Cl_2N_4P_4Pd$ (M = 1197): C, 64.16; H, 6.02; N, 4.68; P, 10.36. Found: C, 63.7; H, 6.2; N, 4.2; P, 10.0%.

[1,5-(*R*,*R*)-Bis(α-methylbenzyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane]bromotricarbonylrhenium(I) (6r). [{ReBr(CO)$_3$(thf)}$_2$] (0.19 g, 0.23 mmol) in 3 mL of DMF was added to a solution of **1r** (0.23 g, 0.45 mmol) in 7 mL of DMF. The next day the solvent was removed in vacuum, **6r** was crystallised from chloroform and white crystals were collected by filtration, washed with chloroform and dried under vacuum. Yield: 0.23 g, 59%, mp 150 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.64 (d, $^3J_{HH}$ = 6.8 Hz, 3H, C′H$_3$), 2.62 (dd, $^2J_{HH}$ = 12.0 Hz, $^2J_{PH}$ = 12.9 Hz, 1H, PCH^{1B}$_2$N), 3.16 (m, 2H, PCH^{2AB}$_2$N), 3.41 (d, $^2J_{HH}$ = 12.7 Hz, 1H, PCH$^{2'B}$$_2$N), 3.70 (d, $^2J_{HH}$ = 12.0 Hz, 1H, PCH^{1A}$_2$N), 3.73 (d, $^2J_{HH}$ = 11.7 Hz, 1H, PCH$^{1'B}$$_2$N), 3.76 (q, $^3J_{HH}$ = 6.8 Hz, 1H, C*H), 4.10 (q, $^3J_{HH}$ = 6.8 Hz, 1H, C*′H), 4.16 (dd, $^2J_{HH}$ = 12.7 Hz, $^2J_{PH}$ = 6.8 Hz, 1H, PCH$^{1'A}$$_2$N), 4.59 (dd, $^2J_{HH}$ = 11.7 Hz, $^2J_{PH}$ = 6.4 Hz, 1H, PCH$^{2'A}$$_2$N), 6.93–7.59 (m, 20H, C_6H_5). ^{13}C{^{1}H} NMR (DMF-d_7): δ 13.31 (br s, CH_3), 18.96 (br s, C′H$_3$), 42.38 (br dd, $^1J_{PC}$ = 33 Hz, $^3J_{PC}$ = 6 Hz, C^1), 46.15 (br dd, $^1J_{PC}$ = 35 Hz, $^3J_{PC}$ = 8 Hz, C$^{2'}$), 48.55 (br dd, $^1J_{PC}$ = 31 Hz, $^3J_{PC}$ = 7 Hz, C^2), 52.72 (br dd, $^1J_{PC}$ = 36 Hz, $^3J_{PC}$ = 6 Hz, C$^{1'}$), 67.47 (t, $^3J_{CP}$ = 10.3 Hz, C*), 67.57 (t, $^3J_{CP}$ = 12.0 Hz, C*′), 128.18 (s, C^{10}), 128.44 (s, C$^{10'}$), 128.54 (s, C^8), 128.74 (s, C$^{8'}$), 128.96 (s, C^9), 129.24 (s, C$^{9'}$), 129.75 (d, $^3J_{CP}$ = 7.9 Hz, C^5), 129.90 (d, $^3J_{CP}$ = 8.3 Hz, C$^{5'}$), 130.87 (d, $^2J_{CP}$ = 7.5 Hz, C^4), 131.11 (d, $^2J_{CP}$ = 7.4 Hz, C$^{4'}$), 131.31 (s, C$^{6,6'}$), 140.93 (s, C^7), 141.56 (s, C$^{7'}$), 189.88, 191.30, 191.73 (CO). C^3 was not observed. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −16.6 (d), −16.9 (d) ($^2J_{PP}$ = 57.8 Hz). a = +13 for **6r** (c = 0.07, $CHCl_3$). IR: ν(CO) = 2028, 1946, 1897 cm^{-1}. Anal. Calc. for $C_{35}H_{36}BrN_2O_3P_2Re$ (M = 860): C, 48.84; H, 4.19; N, 3.26; P, 7.21. Found: C, 49.0; H, 4.3; N, 3.1; P, 6.9%.

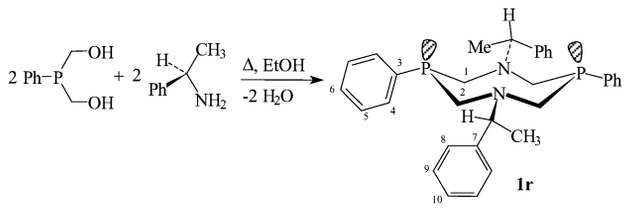
Co-polymerisation of norbornadiene (nbd) and CO. The procedure for studying the kinetics of co-polymerisation of nbd and CO has already been described.[26]

A solution of Pd(CH$_3$COO)$_2$ (11.25 mg, [Pd(CH$_3$COO)$_2$] = 7.2 × 10^{-4} mol l^{-1}), ligand (38 mg, [**1s**/Pd(CH$_3$COO)$_2$] = 1.5), CF_3COOH (0.008 ml) or p-$CH_3C_6H_4SO_3H$ (0.48 mg) in CH_2Cl_2–CH_3OH (58 : 2 ml) and nbd (10 ml) were placed in a 200 ml mechanically stirred steel autoclave, which was then charged with carbon monoxide (p_{CO} = 4.0 MPa).

The reaction mixture was stirred at 54 °C for 6 h, and then the remaining carbon monoxide was vented off, and the co-polymer precipitated by addition of heptane, collected by filtration and dried under vacuum. After co-polymerisation the surface of the autoclave was coated with black Pd. The nbd/CO co-polymer was soluble in chloroform and THF, and insoluble in methanol and acetone. Anal. Calc. for nbd–CO: C, 80.0; H, 6.5. Found: C, 80.0; H 6.5 (co-polymer **7**); C, 80.4; H 6.6 (co-polymer **8**). ^{1}H NMR ($CDCl_3$) (co-polymer **7**): δ 0.9–2.1 (br m, 6.7H, H^{1,4,7}), 2.1–3.5 (br m, 4.7 H, H^{2,3}), 5.8–6.0 (br m, 0.6H, H^2(**B**)), 6.0–6.3 (br s, 1.4H, H^{2,3}(**A**) and H^3(**B**)) (Fig. 4). ^{13}C{H} NMR ($CDCl_3$) (co-polymer **7**): δ 209.7 (br s, C=O), 208.7 (br s, C=O), 138.1 (br m, C^{5,6}(**A**)), 128.6 (br m, C^{5,6}(**B**)), 10–55 (m, C$^{1-4,7}$). IR (KBr) (co-polymer **7**): 1778(w), 1730(w), 1710(s), 1700(s), 1695(w) cm^{-1}. ^{1}H NMR ($CDCl_3$) (co-polymer **8**): δ 0.9–2.1 (br m, 4.6H, H^{1,4,7}), 2.1–3.5 (br m, 2.6 H, H^{2,3}), 6.0–6.3 (br s, 2H, H^{2,3}). ^{13}C{H} NMR ($CDCl_3$) (co-polymer **8**): δ 210.6 (br s, C=O), 209.2 (br s, C=O), 176 (br s, C–O ethereal), 175 (br s, C–O lactone), 135.9 (br m, C^{5,6}) 113.5 (br s, C–O spiroketal), 10–54 (m, C$^{1-4,7}$). IR (KBr) (co-polymer **8**): 1778(s), 1730(w), 1710(w), 1700(s), 1695(s) cm^{-1}.

Results and discussion

Optically active (*R*)- or (*S*)-α-methylbenzylamine underwent condensation reactions with bis(hydroxymethyl)phosphine to give chiral 1,5-(*R*,*R*)- or 1,5-(*S*,*S*)-bis(α-methylbenzyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane (**1r** or **1s**) in good yield (Scheme 1). Compounds **1r** and **1s** are white, air-stable crystalline solids and soluble in common organic solvents



Scheme 1

(CHCl$_3$, CH$_2$Cl$_2$), in contrast to 1,5-diaza-3,7-diphosphacyclooctanes described previously.[5]

^{31}P, ^{1}H, ^{13}C NMR and elemental analysis data are in good agreement with the proposed structure.

In the ^{1}H and ^{13}C NMR spectra of **1** (**1r** or **1s**) the ring methylene groups are inequivalent due to the presence of asymmetric substituents in the 1- and 5-positions of the heterocycle. In the ^{1}H NMR spectrum they are registered as two (AA′)X spin systems and in the ^{13}C spectra as two AMM′XY spin systems. The asymmetric substituents on the nitrogen atoms are equivalent. The protons of the CH and CH$_3$ groups of the α-methylbenzyl moieties appear as a broad quartet and a doublet, respectively.

X-Ray crystallography confirmed the formation of chiral 1,5-(*R*,*R*)-bis(α-methylbenzyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane (**1r**) (Figs. 1 and 2, Tables 1 and 2). The absolute configuration is known due to the *R* configuration of the starting material, although the large esd of the Flack value [−0.01(17)] does not allow an unambiguous assignment of the configuration.

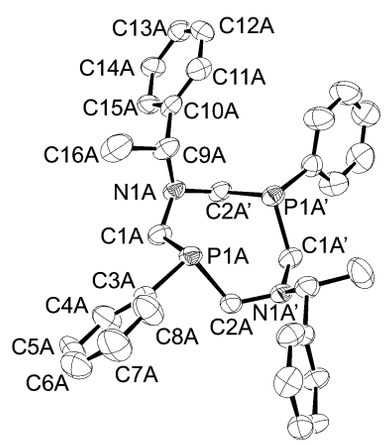


Fig. 1 An ORTEP view of the conformer **1r**′.

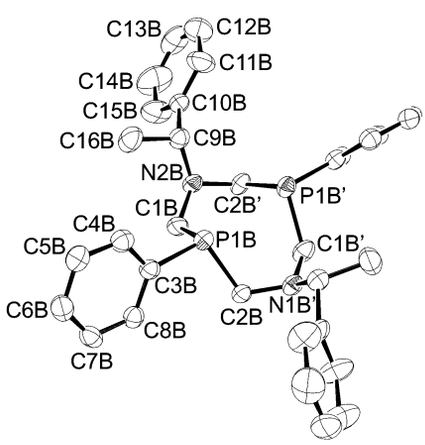
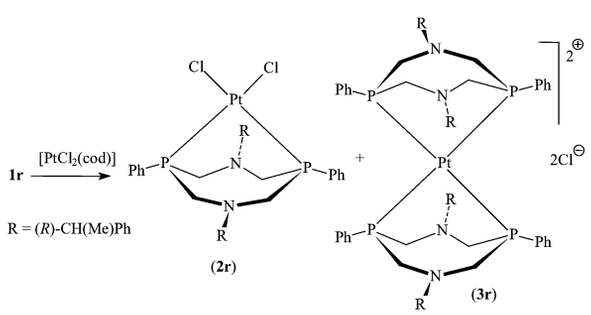


Fig. 2 An ORTEP view of the conformer **1r**″.

Two independent half-molecules are present in the asymmetric unit. Compound **1r** exists as a 1 : 1 mixture of two conformational isomers due to the inequivalence of the P–CH_2–N fragments of the molecule. In conformer **1r′** (Fig. 1) the phenyl ring on the phosphorus atom is almost eclipsed with the P–C^2 bond (torsion angle C(4A)–C(3A)–P(1A)–C(2A) = 19.9°), and in the second conformer **1r″** (Fig. 2) with the P–$C^{1'}$ bond (torsion angle C(8B)–C(3B)–P(1B)–C(1B) = 23.1°). The eclipsed cyclic P–C bond is slightly shorter than the uneclipsed one (1.906 and 1.887 Å for **1r′**, and 1.915 and 1.889 Å for **1r″**). Both isomers have the same "chair-chair" conformation of the bisphosphine heterocycles with nearly parallel phosphorus lone pairs. The P–P distance depends on the conformation along the exocyclic P–C bonds and is noticeably shorter in isomer **1r″** (3.128 Å) in comparison with **1r′** (3.279 Å). The lone pairs of the nitrogen atoms are situated in the equatorial positions. Thus, in the conformation existing in the solid state, only the lone pairs of the phosphorus atoms are situated in positions suitable to trap soft transition metal ions in a chelating fashion.

The high solubility of **1r** or **1s** in organic solvents is unusual for 1,5-diaza-3,7-diphosphacyclooctanes and opens the possibility of designing different chiral complexes of transition metals and catalysts *in situ*. In the reaction mixture of **1r** with one equivalent of [$PtCl_2$(cod)] (cod = cyclooctadiene) in CH_2Cl_2, two signals were observed in the ^{31}P NMR spectrum. One signal was situated close to the signals of *cis*-(1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane)dichloroplatinum(II) (δ ^{31}P −26.3, $^1J_{PtP}$ = 2950 Hz) and the other close to the signals of bis(1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane)platinum(II) dichloride (δ ^{31}P −17.4, $^1J_{PtP}$ = 2302 Hz) described previously.[18,20] The signal of the chelate complex **2r** (δ ^{31}P −24.2, $^1J_{PtP}$ = 2960 Hz) was the minor one (20%), and that of the sterically hindered ionic complex **3r** (δ ^{31}P −10.6, $^1J_{PtP}$ = 2368 Hz) the major one (80%) (Scheme 2). Unconsumed [$PtCl_2$(cod)] crystallised from the reaction mixture.



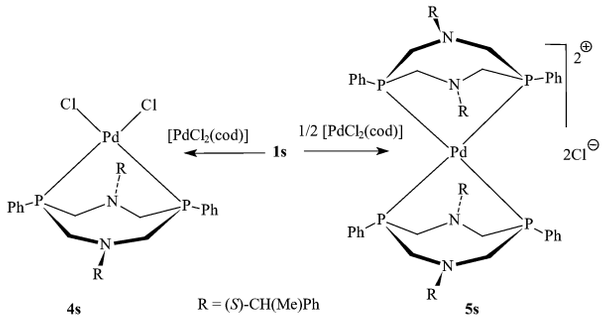
Scheme 2

To obtain **2r** in pure form, a solution of **1r** was added to [$PtCl_2$(cod)] (10% excess) dropwise. In the resulting mixture **2r** was the predominant product (75%), but could not be isolated without **3r**. The salt **3r** could be obtained in high yield in the presence of two equivalents of **1r** or on adding one equivalent of **1r** to the reaction mixture containing **2r**.

Reactions of **1s** with [$PdCl_2$(cod)] gave slightly different results (Scheme 3). In the ^{31}P NMR spectrum of the reaction mixture signals of two complexes were registered. However, the neutral 1 : 1 complex **4s** was the predominant product and could be isolated from the reaction mixture in a pure state. In the ^{1}H NMR spectrum of **4s** two independent (AB)X spin systems for the P–CH_2–N protons were observed, in accordance with inequivalence of C^1 and C^2.

The cationic palladium complex **5s** was synthesised using two equivalents of **1s** and one equivalent of [$PdCl_2$(cod)].

^{1}H and ^{13}C NMR data of the cationic complexes **3r** and **5s** are similar. The chiral substituents on the nitrogen atoms of the

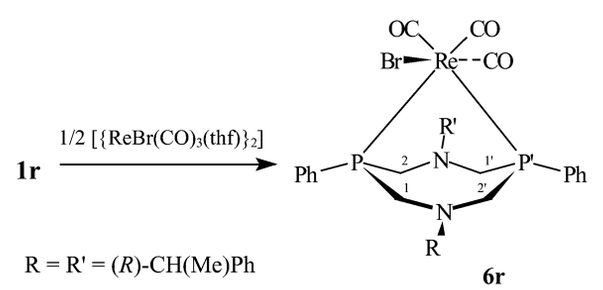


Scheme 3

ligand are equivalent and occupy identical positions above and below the plane of the metallocycle. The P–CH_2–N methylene groups are inequivalent and are observed as two groups of multiplets (broad doublets) in the ^{1}H NMR spectra and two broad singlets in the ^{13}C{^{1}H} spectra of **3r** and **5s**. Signals for the carbon atoms of the phenyl substituent on phosphorus C^4 and C^6 exhibited high- and low-field shifts, respectively, relative to **1**, in accordance with quaternisation of the phosphorus atoms. The signal for C^3 was not observed, perhaps due to the usual low intensity and broadening of signals of carbon atoms connected to phosphorus and coupling with four different phosphorus atoms. The multiplicities of the signals in the coupled ^{13}C NMR spectrum of **5s** confirm the assignments of signals, that is, the heterocyclic ligand in the square-planar complexes **2**–**5** retains the configuration of the starting phosphine **1**.

The noticeable decrease in the stereospecific coupling constants $^2J_{PH}$ for the PCH^A_2N protons of **5s** ($^2J(PH^A) \approx 0$ Hz) in comparison with neutral complex **4s** ($^2J(PH^{A2})$ = 7.2, $^2J(PH^{A1})$ = 6.7 Hz) could be explained in terms of different conformational behaviour of the heterocyclic ligand in the crowded (**5s**) and less crowded (**4s**) transition metal complexes. The same picture was observed for analogous cationic and neutral platinum complexes of 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane.[20]

Reaction of bisphosphine **1r** with [{$ReBr(CO)_3$(thf)}$_2$] in DMF leads to the formation of thin white needles of complex **6r** (Scheme 4). In the IR spectrum of **6r** strong CO absorption bands of the *fac*-$ReBr(CO)_3$ fragment coordinated with the bisphosphine were observed.[27,28] In contrast to complexes **2**–**5** two signals with relatively large coupling constant ($^2J_{PP}$ = 57.8 Hz) were registered in the ^{31}P NMR spectrum of **6r**.



Scheme 4

The signals are situated close to each other (δ −16.6, −16.9) in the low-field region relative to **1**. We suppose that the difference between the two phosphorus atoms in the chelate complex **6r** is connected with the different apical ligands (CO and Br) of the octahedrally coordinated central ion. In accordance with this assumption, the two chiral 1-methylbenzyl substituents on the nitrogen atoms are inequivalent. The CH_3 groups of the α-methylbenzyl moieties are registered as two doublets and the CH groups as two broad quartets in the ^{1}H NMR spectrum of

Table 3 Co-polymerisation activities and MWD of co-polymers nbd–CO

	Acid	[Acid]/[Pd]	W/g g_{Pd}^{-1} h^{-1}	Conv. (%)	M_n	M_w	M_w/M_n
7	**a**	2	10	3.4	820	1100	1.34
8	**b**	5	127	42.8	540	680	1.26

6r. The NMR signals for the protons of the PCH_2N fragments are more complex than those of **1**–**5**. The methylene protons represent four (AB)X systems (one spin system for each proton) in the ^{1}H NMR spectrum, and four doublets of doublets with ^1J(PC) and ^3J(PC) coupling in the $^{13}C\{^1H\}$ spectrum due to the asymmetrical environments of the phosphorus atoms. In addition, there are two sets of lines for each type of phenyl group in the ^{1}H and ^{13}C NMR spectra of **6r**.

The complexity of the ^{1}H NMR spectrum of **6r** prevented a correct conformational analysis. However, the appearance of noticeable ^2J(PH) (6.4–12.9 Hz) coupling constants in most of the (AB)X spin systems of the P–CH_2–N protons indicates that the conformational behaviour of the heterocyclic ligand in compound **6r** is similar to that of **4s** and differs from that of the cationic complexes **3r** and **5s**.

The alternating co-polymerisation of ethylene and carbon monoxide has attracted considerable interest from both academia and industry over the last few decades.[29–33] The presence of carbonyl groups in the polyolefin chain increases the ability of polymers to undergo photo- and biodegradation (at least for the statistical co-polymers) and provides the opportunity to modify the chains to give polymers with unusual combinations of properties. Chiral co-polymers of propene and styrene have been already studied.[34] There is no information about chiral co-polymers of norbornadiene (nbd) and CO.

Catalysts obtained *in situ* from **1s**, $Pd(CH_3CO_2)_2$ and CF_3CO_2H or *p*-$CH_3C_6H_4SO_3H$ catalysed the co-polymerisation of norbornadiene and carbon monoxide. Fig. 3 shows kinetic curves for the co-polymerisation of norbornadiene and carbon monoxide in the presence of two promoters: CF_3COOH or *p*-$CH_3C_6H_4SO_3H$.

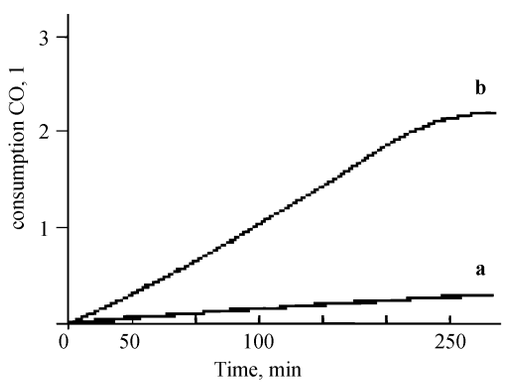


Fig. 3 Kinetic curves of nbd–CO co-polymerisation in the presence of two promoters: CF_3COOH (**a**) and *p*-$CH_3C_6H_4SO_3H$ (**b**)

The reaction rate and yield of co-polymer (see Table 3) are noticeably higher for *p*-$CH_3C_6H_4SO_3H$ **b** (co-polymer **8**) than for CF_3COOH **a** (co-polymer **7**). However the molecular weight of the co-polymer in this case is lower (Table 3).

^{1}H and ^{13}C NMR data give some additional information about co-polymer structures. Co-polymer **8** has mainly *cis* structure **A** (δ $H^{5,6}$ 6.2), and co-polymer **7** is a mixture of *cis* (**A**) and *trans* (**B**) structures (δ $H^{5,6}$ 6.2, 5.9) (Fig. 4). Thus, co-polymerisation in the presence of *p*-$CH_3C_6H_4SO_3H$ proceeds stereoselectively to produce only optically inactive, symmetric (*R*,*S*)-norbornene units. The ratio of integral intensities of aliphatic (H^{1-4} and H^7) and olefinic ($H^{5,6}$) protons (*ca.* 6 for **7** and *ca.* 4 for **8**) are higher than the expected value (3), perhaps due to the participation of both double bonds of nbd in the co-polymerisation. In the ^{13}C NMR spectrum of co-polymer **7** only one broad signal for carbonyl groups was registered, and for co-polymer **8** this signal was accompanied by signals for ethereal (δ 176), lactone (δ 175) and spiroketal (δ 113.5) groups.[35]

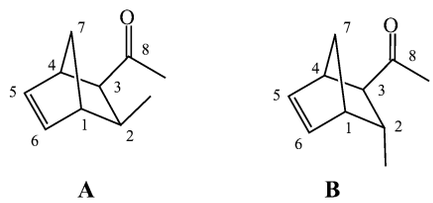


Fig. 4

The appearance of black palladium in the reaction mixture and relatively low efficiency of the catalysts could be explained by the formation of ionic complexes $[PdL_2]^{2+}$ (*cf.* **5s**) in the presence of a weakly nucleophilic anion ($CF_3CO_2^-$ or *p*-$CH_3C_6H_5SO_3^-$). The excess of palladium acetate then decomposes to give black palladium. The activity and selectivity of cationic complexes are low due to the steric hindrance around the palladium atom in cationic complexes.

On the whole, the catalyst systems on the basis of **1s** described here demonstrate rates of co-polymerisation and co-polymer MWDs comparable or higher than those of the best already known catalysts.[36–38] The catalyst affords co-polymers with predominantly *cis*-(*R*,*S*)-norbornene units.

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References

1 *Homogeneous Catalysis with Metal Phosphine Complexes*, ed. L. H. Pignolet, Plenum Press, New York, 1983.
2 *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, VCH, Weinheim, 1996.
3 H. Brunner and W. Zettlmeier, *Handbook of Enantioselective Catalysis with Transition Metal Compounds*, VCH, Weinheim, 1993.
4 K. Kellner and A. Tzschach, *Z. Chem.*, 1984, **24**, 365.
5 B. A. Arbuzov and G. N. Nikonov, *Adv. Heterocycl. Chem.*, 1994, **61**, 60.
6 O. A. Erastov and G. N. Nikonov, *Functional Phosphines and their Derivatives*, Moscow, Nauka, 1986.
7 G. Markl and G. Yu Jin, *Tetrahedron Lett.*, 1981, **22**, 223.
8 G. Markl, G. Yu Jin and Ch. Schoerner, *Tetrahedron Lett.*, 1980, **21**, 1845.
9 K. Kellner, W. Hanke and A. Tzschach, *Z. Chem.*, 1984, **24**, 193.
10 K. Kellner, A. Tzschach, Z. Nagy-Magos and L. Marko, *J. Organomet. Chem.*, 1980, **193**, 307.
11 M. T. Reetz and S. R. Waldvogel, *Angew. Chem.*, 1997, **109**, 870.
12 D. Astruc and F. Chardac, *Chem. Rev.*, 2001, **101**, 2991.
13 P. Arya, N. V. Rao and J. Singkhonrat, *J. Org. Chem.*, 2000, **65**, 1881.
14 D. E. Berning, K. Katti, C. L. Barnes and W. A. Volkert, *J. Am. Chem. Soc.*, 1999, **121**, 1658.
15 S. V. Bobrov, A. A. Karasik and O. G. Sinyashin, *Phosphorus, Sulfur Silicon*, 1999, **144–146**, 289.
16 A. A. Karasik and G. N. Nikonov, *Z. Obsch. Khim.*, 1993, **63**, 2775 (in Russian).

17 A. A. Karasik, O. G. Sinyashin, J. Heinicke and E. Hey-Hawkins, *Phosphorus, Sulfur Silicon*, 2002, **177**, 1469.
18 B. A. Arbuzov, A. A. Karasik and G. N. Nikonov, *Bull. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 253.
19 A. A. Karasik, G. N. Nikonov and A. S. Dokuchaev, *Russ. J. Coord. Chem.*, 1994, **20**, 300.
20 A. A. Karasik, S. V. Bobrov and G. N. Nikonov, *Russ. J. Coord. Chem.*, 1995, **21**, 574.
21 A. A. Karasik, I. O. Georgiev, R. I. Vasiliev and O. G. Sinyashin, *Mendeleev Commun.*, 1998, 140.
22 A. A. Karasik, I. O. Georgiev, O. G. Sinyashin and E. Hey-Hawkins, *Polyhedron*, 2000, **19**, 1455.
23 A. A. Karasik, I. O. Georgiev, E. I. Musina, J. Heinicke and O. G. Sinyashin, *Polyhedron*, 2001, **20**, 3321.
24 SADABS: G. M. Sheldrick, SADABS, Program for Scaling and Correction of Area-detector Data, Göttingen, 1997.
25 SHELX97: SHELXS97 and SHELXL97 – Programs for Crystal Structure Analysis. G. M. Sheldrick, University of Göttingen, 1998.
26 G. P. Belov, E. G. Chepaikin, A. P. Bezruchenko and V. I. Smirnov, *Vysokomol. Soedin. Ser. A*, 1993, **35**, 1585.
27 D. H. Gibson, H. He and M. S Mashuta, *Organometallics*, 2001, **20**, 1456.
28 R. Schibli, K. V. Katti, W. A. Volkert and C. L. Barnes, *Inorg. Chem.*, 2001, **40**, 2358.
29 C. Bianchini and A. Meli, *Coord. Chem. Rev.*, 2002, **225**, 35.
30 E. Drent and P. H. M. Budzelaar, *Chem. Rev.*, 1996, **96**, 663.
31 G. P. Belov, *Polym. Sci., Ser. B.*, 1998, **40**, 89.
32 G. P. Belov, *Polym. Sci., Ser. C.*, 2001, **43**, 46.
33 G. P. Belov, *Kinet. Catal.*, 2001, **42**, 301.
34 W. R. Pousch, J. M. Hawkins and R. H. Grubbs, *Chemtracts: Org. Chem.*, 1988, **1**, 21.
35 M. D. E. Forbes, S. R. Ruberu, D. Nachtigallova, K. D. Jordan and J. C. Barborak, *J. Am. Chem. Soc.*, 1995, **117**, 3946.
36 T. Kawaguchi, M. Kanno, T. Yanagihara and Y. Inoue, *J. Mol. Catal.*, 1999, **143**, 253.
37 D.-J. Liaw and J.-S. Tsai, *J. Polym. Sci. Part A. Polym. Chem.*, 1997, **35**, 1157.
38 S.-W. Zhang, T. Kaneko and S. Takahashi, *Macromolecules*, 2000, **33**, 6930.