DALTON

New Schiff bases derived from *trans*-pyrazolylcyclohexanol: synthesis, co-ordination chemistry and structural features‡

Michael Barz, Monika U. Rauch and Werner R. Thiel*,†

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4,
D-85747 Garching, Germany

Transformation of the OH function of *trans*-2-(pyrazol-1-yl)cyclohexan-1-ol into an amino group was achieved by various methods with inversion of the reaction centre and provided access to new polydentate Schiff bases bearing phenol, pyridine and furan donors. The co-ordination chemistry of these bases was investigated for Pd^{II}, Re^{I} and Re^{V}. It was shown by means of NMR spectroscopy that the special stereochemical situation of the 1,2-*cis*-configurated cyclohexane backbone allows a flexible adaptation to different co-ordination conditions. On the other hand, the rigid asymmetrically substituted cyclohexane ring is responsible for an asymmetric arrangement of the donor fragments at the metal centre, which is required for applications of these compounds in enantioselective catalysis.

During the last 25 years the development of new chiral compounds has led to rapid progress in the area of enantioselective catalysis. Especially the introduction of C_2-symmetric phosphanes gave rise to a multitude of new catalytic and enantioselective reactions, like hydrogenations, isomerisations or hydroformylations.[2] Besides these new chiral phosphanes, chiral nitrogen-containing compounds play an increasingly important role in enantioselective catalysis. An outstanding example is the enantioselective *cis* hydroxylation of olefins, catalysed by osmium complexes in the presence of cinchona alkaloids.[3] Additionally, compounds bearing nitrogen atoms as donor centres have been applied for enantioselective hydrogenations (Co, Rh), hydrosilylations (Rh), the synthesis of chiral cyclopropanes (Co, Cu, Rh), stereoselective Diels–Alder reactions (Al, Mg, Fe), alkylation of ketones with dialkylzinc compounds, coupling reactions [MgR(X) and Pd], oxidations (Mo, V, Mn) and olefin metathesis (Mo).[4]

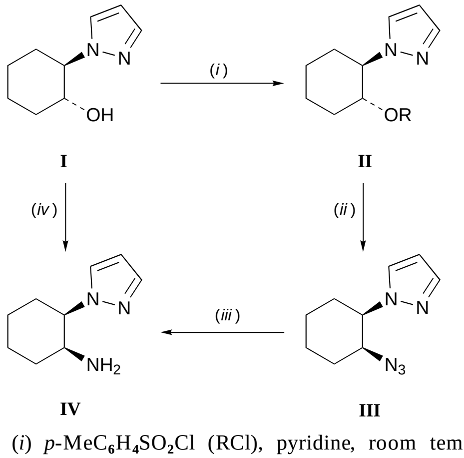
In our group the ring-opening reaction of prochiral, cyclic epoxides with various nucleophiles is used for the synthesis of new cycloalkanol ligands bearing two stereocentres at a rigid cyclic backbone. Pyrazoles and imidazoles, for example, give exclusively the corresponding *trans*-substituted 2-(diazol-1-yl)-cycloalkan-1-ols. We previously demonstrated for the corresponding phosphanes[1] that the cyclic backbone forces the (bulky) substituents at the donor moieties into a pseudo-C_2-symmetrical arrangement around the metal centre, as is known for complexes of C_2-symmetric diphosphanes.[2c] Obviously, racemic mixtures are obtained in the ring-opening reaction, which have to be separated. We therefore recently worked out a procedure for the separation of the enantiomers of 2-(pyrazol-1-yl)cyclohexan-1-ol **I** by an enzymatic kinetic resolution,[5] which gives access to a multitude of enantiomerically pure 1,3-diaminoalcohols. Besides the co-ordination chemistry of these aminoalcohols, which turned out to be ideal ligands for the complexation of first-row transition metals,[6] we are interested in these compounds as starting materials for the synthesis of other chiral chelates like Schiff bases, diamines or phosphorus donors.

In all these cases the molecular geometry of the resulting transition-metal complexes depends on the absolute configurations of the stereocentres and on the particular conformation of the cycloalkane ring. Additionally, if several donor centres can compete for a co-ordination site, fluxional behaviour may be observed. In the present paper we report the synthesis of Schiff bases derived from racemic **I** and their co-ordination chemistry with high- and low-valent transition-metal fragments with special regard to the conformational behaviour of the cyclohexane ring system.

Results and Discussion

Ligands

For the synthesis of new Schiff bases, compounds known to be excellent donors for transition and main-group elements,[7] the OH functionality of **I** had to be transformed into an amino group. Since the second stereocentre at the cyclohexane ring will not be affected during the synthetic procedure, the stereoselectivity of the appropriate transformations can easily be determined by NMR spectroscopy. The conversion of the alcohol **I** into the corresponding amine **IV** was realised by two different routes (Scheme 1): *via* a classical nucleophilic substitution reaction or a Mitsunobu amination. The tosylate **II**, accessible in good yields by reaction of **I** with toluene-*p*-sulfonyl chloride,[8] is converted in a S_N2 type reaction with sodium azide in dmf solution at 160 °C into the *cis*-

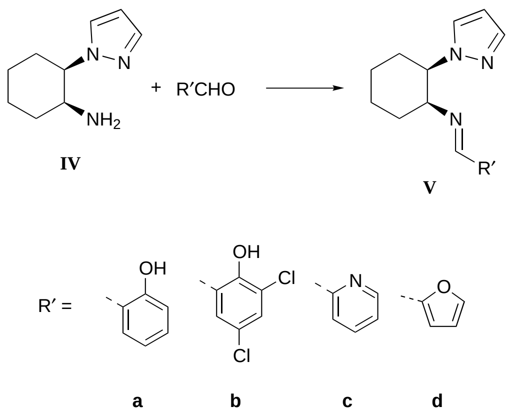


Scheme 1 (*i*) *p*-$MeC_6H_4SO_2Cl$ (RCl), pyridine, room temperature (r.t.), 48 h; (*ii*) NaN_3, dimethylformamide (dmf), 160 °C, 3 h; (*iii*) $LiAlH_4$, diethyl ether, reflux, 3 h; (*iv*) (*a*) $EtO_2CN{=}NCO_2Et$, PPh_3, tetrahydrofuran (thf), 24 h, r.t.; (*b*) N_2H_4, methanol, HCl, reflux, 14 h

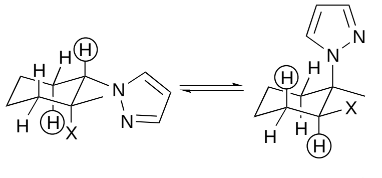
---

† E-Mail: thiel@arthur.anorg.chemie.tu-muenchen.de

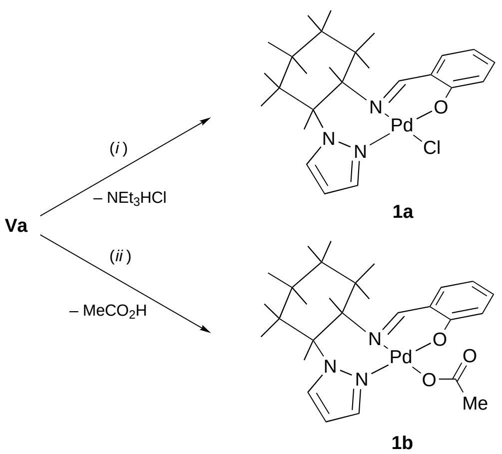
‡ Cycloalkanes as ligand backbones. Part 3.[1]



Scheme 2



Scheme 3 The equilibrium between the two conformers of compounds **III**, **IV** and **Va**, **Vb**



Scheme 4 (*i*) $[PdCl_2(PhCN)_2]$, NEt_3; (*ii*) $Pd(O_2CMe)_2$

configurated azide **III**.[9] Irrespective of the high reaction temperatures, **III** is formed in more than 99% diastereomeric excess (inversion at the reaction centre). It can be used as a chelate for complexation of transition metals, and its stereochemistry (1,2-*cis* substitution) was demonstrated by a X-ray analysis of the corresponding $CuCl_2$ complex.[6] Reduction of **III** with $LiAlH_4$ in thf solution leads to the desired amine **IV**.[10] In an alternative reaction sequence, the alcohol **I** is converted into the amine **IV** by the so-called Mitsunobu reaction, which also proceeds with more than 99% diastereomeric excess under inversion at the reaction centre.[11]

Starting from diastereomerically pure compound **IV**, the Schiff bases **Va**–**Vd** are obtained in almost quantitative yields (Scheme 2).[12] In the case of free **Va** and **Vb**, ^1H NMR spectroscopy revealed an interaction between the phenolic hydrogen atoms and the imine nitrogen as the resonances of these protons are shifted to lower field (δ 13.57 and 14.69).

As previously shown by means of NMR spectroscopy and X-ray analysis,[5] the 1,2-*trans*-disubstituted cyclohexane ring of **I** occupies the energetically favourable chair conformation with both the pyrazolyl and the hydroxy substituent orientated in equatorial positions, minimising axial–axial interactions. The same situation is found for the corresponding tosylate **II**. During the formation of the amine **IV**, described above, inversion at the reaction centre takes place. This results in a 1,2-*cis*-configurated cyclohexane ring, a common structural feature for **III**, **IV**, the imines **V** and the corresponding transition-metal complexes discussed later on. These compounds can now exist as a mixture of two conformers, which should be in equilibrium in solution. In these conformers the pyrazolyl group either occupies an equatorial or an axial position (opposite orientation of the second substituent X, Scheme 3).

Proton NMR spectroscopy allows one to distinguish between these conformers, as in each case only one of the protons in 1 or 2 position will show one strong *trans* coupling of about 12 Hz, while the other proton–proton couplings are weak (*ca.* 2–3 Hz) due to dihedral angles (H−C−C−H) of about 60°. Molecular mechanics (MM) calculations, using the MM2 force field implemented in CHEM3D,[13] showed that the equatorial orientation of the pyrazolyl moiety should be favoured by about 6–8 kJ mol^{-1}, depending on the second substituent, and a barrier of about 30 kJ mol^{-1} should hinder the interconversion of the conformers. While the latter value corresponds to reported data,[14] the calculated energy differences between the conformers should be underestimated by some kJ mol^{-1}. In the case of the pure organic compounds **III**–**V**, we only observed one conformer (>98%), bearing an equatorial pyrazolyl group, by NMR spectroscopy.

Depending on the metal fragment, the imines **V** can co-ordinate in a mono- (excluded for reasons of complex stability), bi- or tri-dentate mode. Additionally, the geometry of the cyclohexane backbone of the ligands will be determined by the specific co-ordination pattern, as the barriers to ring interconversion and the energy differences between the conformers described above are low.

Metal complexes

Substitution of the labile benzonitrile ligands of $[PdCl_2(PhCN)_2]$ by compound **Va** in the presence of NEt_3 results in tridentate co-ordination of the ligand. While one chloro ligand is displaced by the deprotonated phenol fragment, the second chloride occupies the fourth co-ordination site of the square-planar palladium centre (complex **1a**, Scheme 4). If palladium acetate is used as the starting material, the corresponding acetato complex **1b** is obtained even in the absence of a base by simple elimination of acetic acid. Proton NMR spectroscopy reveals the stereochemistry of the cyclohexane ring in **1a**, **1b**: in both cases, a large coupling constant is observed for the ring proton geminal to the imine nitrogen, indicating an equatorial orientation of the imine fragment and an axial orientation of the pyrazole moiety, which is opposite to the geometry of the free imine. There is no special influence of the chloro or the acetato ligand on the geometry of the ligand backbone. One single C=O absorption at 1716 cm^{-1} in the infrared spectrum of **1b** is characteristic for a η^1-co-ordinated acetato ligand.

By slowly cooling a saturated acetonitrile solution of the palladium complex **1a** orange plates are obtained. The complex crystallizes in the monoclinic, centric space group $P2_1/c$ with one additional solvent molecule per formula unit, which does not co-ordinate to the palladium centre. Fig. 1 presents the molecular structure, characteristic bond lengths and angles are given in Table 1, and further crystallographic and experimental details in Table 2. The distances between the square-planar palladium centre and the four ligands are comparable to those of analogous compounds.[17] Five different ring systems are responsible for the molecular structure of **1a**. Three (pyrazole, cyclohexane, phenol) originate from the chelate **Va**, while the two new rings are formed by co-ordination of the metal atom by three donor centres of the chelate. The first three ring systems show normal conformations after co-ordination. While the pyrazole and the phenol ring are almost planar, the cyclohexane ring is in the energetically favourable chair conformation. In that conformation the pyrazole moiety is orientated in an axial, and the nitrogen atom of the imine in an equatorial,

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

Pd–Cl	2.3181(7)	O–C(16)	1.313(3)
Pd–O	1.977(2)	N(3)–C(9)	1.483(3)
Pd–N(2)	2.010(2)	N(3)–C(10)	1.298(3)
Pd–N(3)	1.988(2)		
Cl–Pd–O	84.32(5)	O–Pd–N(3)	93.24(8)
Cl–Pd–N(2)	90.54(6)	N(2)–Pd–N(3)	91.92(8)
Cl–Pd–N(3)	177.16(6)	O–Pd–N(2)	174.83(8)
Pd–N(3)–C(9)	121.9(2)	Pd–N(3)–C(10)	123.4(2)
Pd–O–C(16)	125.4(2)	C(9)–N(3)–C(10)	114.7(2)

Table 2 Crystallographic data for complex **1a**

Formula	$C_{16}H_{18}ClN_3OPd{\cdot}CH_3CN$
M_r	451.224
Crystal system	Monoclinic
Crystal dimensions/mm	0.40 × 0.16 × 0.08
Space group	$P2_1/c$ (no. 14)
a/Å	9.120(1)
b/Å	19.626(2)
c/Å	10.903(1)
β/°	108.19(1)
U/Å^3	1854.0(3)
D_c/g cm^{-3}	1.617
Z	4
F(000)	912
μ/cm^{-1}	11.6
θ Range/°	2.2–25.06
T/°C	−80
Absorption correction	Ref. 16(*a*)
Data measured	14 240
Unique data	3232
Reflections used [$I > 2\sigma(I)$]	2949
No. parameters	310
Residual electron density/e Å^{-3}	+0.36, −0.63
R^a	0.0282
$wR2^b$	0.0776
Goodness of fit	1.09

^{a} $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2F_o^2 + (0.0555P)^2 + 0.68P]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.[16b]

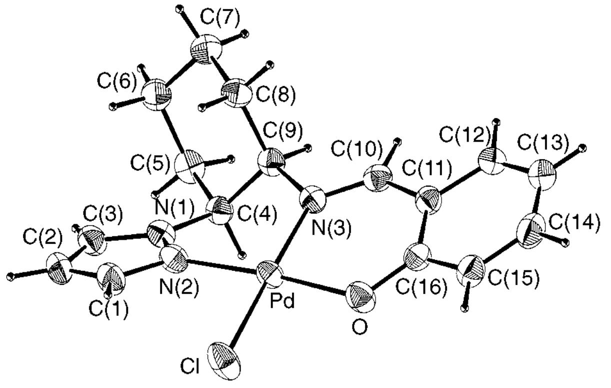
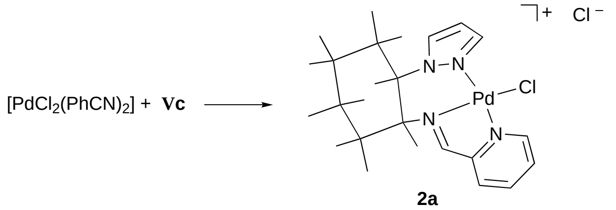


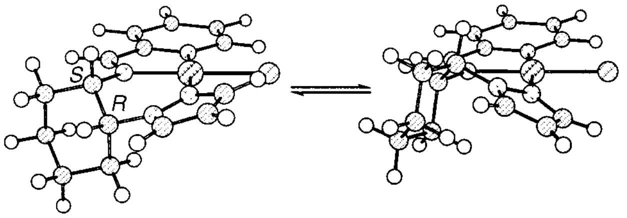
Fig. 1 A PLATON plot[15] of complex **1a** (the additional acetonitrile molecule is omitted). Thermal ellipsoids are at the 50% probability level

position as observed in solution. The pyrazole ring is twisted about 21° around the axis Pd–N(2), which leads to a remarkable asymmetry in the co-ordination sphere of palladium. Owing to the *cis* arrangement of the substituents at the cyclohexane ring, the six-membered ring formed by co-ordination of N(2) and N(3) to palladium is found in a skewed-boat conformation. The least-squares planes of the cyclohexane ring and the pyrazole are orientated almost perpendicular (*ca.* 83°) to each other. Obviously, *cis* substitution of cyclohexane ring systems is an ideal tool for generation of asymmetric ligand spheres at catalytically active metal centres. We are now looking for derivatives of our compounds, bearing bulky substituents at C(1) (pyrazole) or C(15) (phenol), which should lead to a further increase in steric demand at the metal atom.

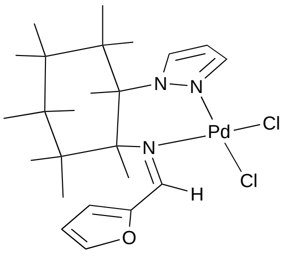


2a

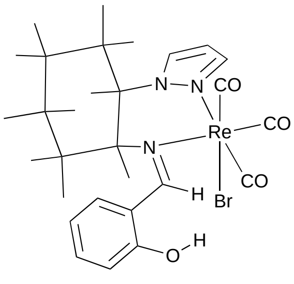
Scheme 5



Scheme 6 Fluxional process equilibrating the two isomers of the cation of complex **2a**



2b

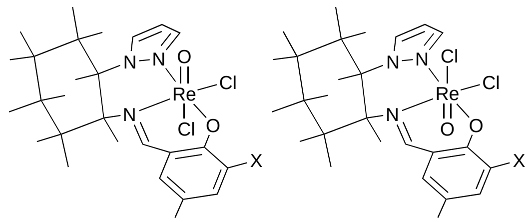


3

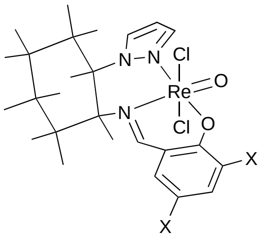
Reaction of the pyridine-substituted compound **Vc** with $[PdCl_2(PhCN)_2]$ leads, by displacement of one chloro ligand, to the square-planar complex **2a** (Scheme 5). The cationic nature of this species, bearing a tridentate ligand, is revealed by conductivity measurements (Λ_m = 62 S cm^2 mol^{-1}, 25 °C, 0.001 mol dm^{-3} in dmf). Additionally, mass spectrometric investigations [fast atom bombardment (FAB)] only showed the isotope pattern of the cationic species PdL(Cl)$^+$. In the ^{1}H NMR spectrum all resonances are shifted to lower field, with respect to **1a** and **Vc**, which is in accordance with the cationic nature of the palladium complex. At room temperature broad signals are observed, indicating a dynamic process in the ligand sphere. For a detailed investigation of this process we carried out NMR experiments in the temperature range between +20 and −80 °C. At low temperatures (< −40 °C) the resonances of two cationic palladium complexes, observed in a 1 : 1 ratio, can be identified. Two-dimensional NMR experiments allowed a complete assignment of the signals and, in combination with data from experiments at various temperatures, the calculation of the energy of activation for this dynamic process ($\Delta G^\ddagger$ = 57 ± 2 kJ mol^{-1}). Since NMR spectroscopy clearly demonstrates a tridentate co-ordination for both species, the only explanation possible for the nature of this process is an inversion of the cyclohexane ring, as shown in Scheme 6.

Replacing the pyridine fragment of compound **Vc** by the weaker donating furan group of **Vd** generates a new system, which could co-ordinate either in a bidentate mode or as a tridentate chelate with a labile donor site.[18] The composition of the corresponding dichloropalladium complex **2b**, obtained by reaction of **Vd** with $[PdCl_2(PhCN)_2]$, is verified by elemental analysis; NMR spectroscopic investigations were impossible as the compound is completely insoluble in most organic solvents, with the exception of hot dimethylformamide and hot dimethyl sulfoxide, wherein decomposition occurs.

Refluxing $[ReBr(CO)_5]$, synthesized from $[Re_2(CO)_{10}]$ and bromine,[19] with 1 equivalent of compound **Va** in thf solution, yields the octahedral rhenium(I) complex **3**. Even in its depro-

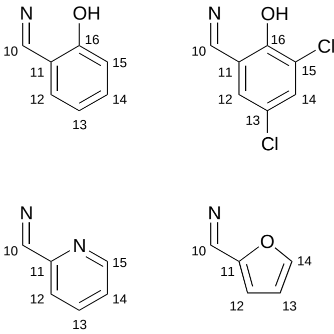


Isomer **A** and **B**



Isomer **C**

4a X = H
4b X = Cl



Scheme 7

tonated form **Va** is not able to replace the bromo ligand at the low-valent rhenium centre. From NMR and IR investigations it is clear that the carbonyl ligands are co-ordinated facially, as is known for other complexes of the type $[ReBr(CO)_3(L-L)]$ (L−L = bidentate chelate ligand).[20] If the donor sites of the chelate ligand are inequivalent, as they are in our case, the metal becomes a centre of chirality. In combination with the racemic ligand **Va**, the introduction of a new chiral centre should result in the formation of two diastereomeric species, which are not observed in the NMR spectra of **3**. At the moment we do not know why only one of the diastereomers is formed selectively. Since the resonance of the OH proton is observed fairly deshielded at δ 10.87, a weak hydrogen interaction of the OH group and the bromo ligand may be the reason for this behaviour. If this is true, the imine fragment must be orientated almost perpendicular to the phenol group. This would minimise π interactions between these fragments and lead to a low-field shift of the resonance of the imine proton, which is indeed observed at δ 9.80. For steric reasons, the imine group should be configurated, as shown in Scheme 6, to prevent interaction of the bulky phenol group with the equatorial carbonyl ligand in the *cis* position, a fact which also may be responsible for the deshielding of the imine proton.

Switching to the more Lewis-acidic rhenium(V) precursor $[NEt_4][ReOCl_4]$ results in a tridentate co-ordination mode of the chelates **Vc**, **Vb** with oxygen as well as both nitrogen atoms binding to rhenium. The octahedral complexes **4a**, **4b** are obtained in high yields. For steric reasons, the three donor centres of the ligand co-ordinate meridionally. This mode allows the formation of three isomers, one (**C**) with the oxo ligand *trans* to the imine nitrogen. In the other isomers one chloro ligand is *trans* to the imine nitrogen and the oxo ligand is in the *cis* position, which results in the generation of a new chiral centre, the metal atom. As we use racemic mixtures of **Va**, **Vb** these isomers are diastereomers (**A** and **B**). All three isomers can be observed by NMR spectroscopy. While the resonances of the diastereomeric complexes **A** and **B** can be assigned without problems (see Experimental section), the minor (*ca.* 10% of intensity) product **C** can be clearly identified by a characteristic resonance for the imine proton at about δ 9.27, indicating the strong *trans* influence of the oxo ligand. In contrast to the square-planar palladium(II) complexes **1a**, **1b**, the geometry of the cyclohexane backbone in **4a**, **4b** switches back to that of the free Schiff bases: pyrazole in equatorial, imine in axial orientation.

As described in this paper, the 1,2-*cis*-substituted cycloalkane ring system allows detailed investigations into stereochemical features of the ligands and transition-metal complexes. Its conformational flexibility, in combination with the rigidity of the six-membered ring, can readily be compared with the structural characteristics of *e.g.* C_2-symmetric phosphanes like the well known 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl system.[2c] We therefore are now looking out for catalytic applications of the enantiomerically pure Schiff bases.

Experimental

The compounds *rac-trans*-2-(pyrazol-1-yl)cyclohexan-1-ol **I**,[5] $[PdCl_2(PhCN)_2]$,[21] $[ReBr(CO)_5]$[19] and $[NEt_4][ReOCl_4]$[22] were synthesized according to published procedures. All other starting materials were from Aldrich and used without further purification. The NMR (Bruker DPX 400), infrared (Perkin-Elmer 1600 Series FTIR) and mass spectra (Hewlett-Packard HP 5890 gas chromatograph and mass-selective detector HP 5970, Finnigan MAT 90) and all elemental analyses were carried out at the Anorganisch-chemisches Institut der TU München. The assignments of the NMR spectra of the 2-(pyrazol-1-yl)-cyclohexyl moiety were made according to Fig. 1, those of the imine residues according to Scheme 7.

Syntheses

***rac-trans*-2-(Pyrazol-1-yl)cyclohexyl toluene-*p*-sulfonate II.** Compound **I** (20.0 g, 120 mmol) and toluene-*p*-sulfonyl chloride (22.9 g, 120 mmol) were dissolved in $CHCl_3$ (150 cm^3) at 0 °C. Pyridine (40 cm^3) was added dropwise and the reaction mixture stirred for 2 d at room temperature. The solution was extracted three times with water (30 cm^3), the organic layer separated, dried over $MgSO_4$ and the solvent removed *in vacuo*. After washing the colourless residue with diethyl ether (50 cm^3) and pentane it was recrystallised from ethyl acetate. Colourless crystals, m.p. 154–156 °C, yield 17.1 g (45%) (Found: C, 59.95; H, 6.2; N, 8.75; S, 10.6. $C_{16}H_{20}N_2O_3S$ requires C, 60.0; H, 6.3; N, 8.75; S, 10.0%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1192s, 1177vs (SO_2); δ_H(250.13 MHz, 25 °C, $CDCl_3$) 7.35 [d, $^3J(H_oH_m)$ 8.0, H_o], 7.23 [d, $^3J(H^1H^2)$ 1.5, H^1], 7.15 [d, $^3J(H^2H^3)$ 2.5, H^3], 7.12 (d, H_m), 5.99 (dd, H^2), 4.69 [dt, $^3J(H^8{}_{eq}H^9)$ 5.1, $^3J(H^4H^9)$ 10.2, $^3J(H^8{}_{ax}H^9)$ 10.2, H^9], 3.99 [dt, $^3J(H^4H^5{}_{eq})$ 7.0, $^3J(H^4H^5{}_{ax})$ 10.2 Hz, H^4], 2.36 (3 H, s, CH_3) and 2.44–1.34 (8 H, 5m, CH_2); δ_C(100.62 MHz, 25 °C, $CDCl_3$) 144.0 (*ipso*-C), 139.2 (C^1), 133.3 (C_p), 129.5 (C_o), 129.2 (C^3), 127.5 (C_m), 104.7 (C^2), 82.5 (C^9), 63.7 (C^4), 32.7 (C^8), 31.8 (C^5), 24.3 (C^6), 23.8 (C^7) and 21.5 (CH_3); *m/z* (electron impact, EI) 320 (1, M^+), 256 (6, $M - SO_2$), 228 (6, $M - C_7H_8$), 171 (53, $C_7H_7O_3S$), 165 (27, $M - C_7H_7O_2S$), 155 (10, $C_7H_8O_2S$), 148 (74, $M - C_7H_8O_3S$), 121 (8, $C_3H_3N_2–C_4H_6$), 120 (14, $C_3H_3N_2–C_4H_5$), 119 (12, $C_3H_3N_2–C_4H_4$), 107 (30, $C_3H_3N_2–C_3H_4$), 91 (63, C_7H_7), 81 (37, $C_3H_3N_2–CH_2$), 77 (9, C_6H_5), 69 (100, $C_3H_5N_2$), 55 (8, C_4H_7), 51 (6, C_4H_3) and 41 (36%, C_3H_5).

***rac-cis*-1-(2-Azidocyclohexyl)pyrazole III.** A mixture of compound **II** (4.00 g, 12.5 mmol) and sodium azide (6.50 g, 100 mmol) in dry dmf (50 cm^3) was heated to reflux for 3 h. After completion of the reaction, water (50 cm^3) was added and the resulting orange solution extracted three times with diethyl ether (30 cm^3). The combined organic layers were extracted three times with water (30 cm^3), dried over $MgSO_4$ and the solvent removed *in vacuo*. The product was obtained as a pale yellow oil, which solidifies at −34 °C. Yield 1.80 g (75%) (Found: C, 56.4; H, 6.8; N, 36.75. $C_9H_{13}N_5$ requires C, 56.55; H, 6.85; N, 36.6%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 2110vs (N_3); δ_H(400.13 MHz, 25 °C, $CDCl_3$) 7.51 [d, $^3J(H^1H^2)$ 1.5, H^1], 7.45 [d, $^3J(H^2H^3)$ 2.5, H^3], 6.25 (dd, H^2), 4.32 [dt, $^3J(H^4H^9)$ 3.4, $^3J(H^4H^5_{eq})$ 3.4, $^3J(H^4H^5_{ax})$ 12.6, H^4], 4.20 [br, $^3J(H^8_{ax}H^9) = {}^3J(H^8_{eq}H^9)$ *ca.* 2–3 Hz, H^9] and 2.12–1.37 (8 H, 6m, CH_2); δ_C(100.62 MHz, 25 °C, $CDCl_3$) 139.2 (C^1), 127.0 (C^3), 105.2 (C^2), 62.5, 62.2 (C^4, C^9), 29.3 (C^5), 25.5, 24.7 (C^8, C^6) and 19.5 (C^7); *m/z* (EI) 191 (1, M^+), 163 (3, $M - N_2$), 149 (1, $M - N_3$), 121 (3, $C_3H_3N_2$–C_4H_6), 120 (4, $C_3H_3N_2$–C_4H_5), 119 (6, $C_3H_3N_2$–C_4H_4), 107 (4, $C_3H_3N_2$–C_3H_4), 95 (8, $C_3H_3N_2$–C_2H_4), 81 (16, $C_3H_3N_2$–CH_2), 69 (24, $C_3H_5N_2$), 68 (15, $C_3H_4N_2$), 67 (10, $C_3H_3N_2$) and 41 (26%, C_3H_5).

***rac*-*cis*-1-(2-Aminocyclohexyl)pyrazole IV.** *Method A, reduction of* **III**. A solution of compound **III** (6.9 g, 36 mmol) in diethyl ether (50 cm^3) was added dropwise to a suspension of $LiAlH_4$ (2.1 g, 55 mmol) in diethyl ether (250 cm^3) and the resulting mixture refluxed for 3 h. The reaction was quenched by the addition of water (1 cm^3), the resulting precipitate was filtered off, the filtrate dried over Na_2SO_4 and the solvent removed *in vacuo*. The product was obtained as a colourless oil. Yield 3.2 g (53%).

Method B, from compound **I**. A solution of compound **I** (6.7 g, 40 mmol) in dry thf (50 cm^3) and $EtO_2CN_2CO_2Et$ (6.3 cm^3, 40 mmol) were added dropwise and simultaneously to a solution of phthalimide (5.9 g, 40 mmol) and PPh_3 (10.5 g, 40 mmol) in dry thf (200 cm^3) under a nitrogen atmosphere. The reaction mixture was stirred at 20 °C for 1 d and the solvent removed *in vacuo*. After dissolution of the residue in methanol (200 cm^3), hydrazine hydrate (80%, 4.9 cm^3, 80 mmol) was added and the mixture refluxed for 7 h. Concentrated hydrochloric acid (6 cm^3) was added and the mixture refluxed for 7 h. A colourless precipitate formed, which was filtered off and rinsed with dilute hydrochloric acid. The combined aqueous solutions were extracted with $CHCl_3$ (7 × 30 cm^3) and Et_2O (4 × 30 cm^3) and then treated with saturated NaOH until pH > 13. A brownish oil separated, which was extracted with diethyl ether (4 × 30 cm^3). The combined organic layers were washed with brine (4 × 30 cm^3) and dried over $MgSO_4$. The solvent was removed *in vacuo* to yield a yellow oil. Kugelrohr distillation gave the pure amine **IV** as a colourless oil. Yield 3.70 g (56%). $\tilde{\nu}_{max}$/cm^{-1} ($CHCl_3$) 3372m and 3300m (NH_2); δ_H(400.13 MHz, 25 °C, $CDCl_3$) 7.43 [d, $^3J(H^1H^2)$ 1.5, H^1], 7.38 [d, $^3J(H^2H^3)$ 2.0, H^3], 6.15 (dd, H^2), 4.17 [ddd, $^3J(H^4H^9)$ 3.5, $^3J(H^4H^5_{eq})$ 3.5, $^3J(H^4H^5_{ax})$ 12.0, H^4], 3.41 [br, $^3J(H^8_{ax}H^9) = {}^3J(H^8_{eq}H^9)$ *ca.* 2–3 Hz, H^9] and 2.15–1.24 (10 H, 6m, CH_2, NH_2); δ_C(100.62 MHz, 25 °C, $CDCl_3$) 138.6 (C^1), 127.2 (C^3), 104.4 (C^2), 63.4 (C^4), 50.1 (C^9), 31.5 (C^5), 24.7, 24.6 (C^8, C^6) and 18.9 (C^7); *m/z* (EI) 165 (1, M^+), 81 (34, $C_3H_3N_2$–CH_2), 69 (61, $C_3H_5N_2$), 55 (9, C_4H_7), 41 (35, C_3H_5), 30 (33, CH_2NH_2), 28 (100, N_2) and 27 (28%, C_2H_3).

Schiff bases V (general procedure). An equimolar solution of compound **IV** and of the appropriate aromatic aldehyde in ethanol (200 cm^3) was refluxed for 2 h. The solvent was removed and pentane added to the resulting yellow oil. With the exception of **Vc**, the Schiff bases crystallised after 24 h at −28 °C. Yields 70–90%.

***rac*-*cis*-2-[2-(Pyrazol-1-yl)cyclohexyliminomethyl]phenol Va.** (Found: C, 70.95; H, 7.0; N, 15.55; O, 6.45. $C_{16}H_{19}N_3O$ requires C, 71.35; H, 7.1; N, 15.6; O, 5.95%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3428vs (OH), 1626vs (C=N); δ_H(400.13 MHz, 25 °C, $CDCl_3$) 13.57 (s, OH), 7.66 (s, H^{10}), 7.45 [d, $^3J(H^1H^2)$ 1.8, H^1], 7.26 [ddd, $^3J(H^{14}H^{15})$ 8.2, $^3J(H^{13}H^{14})$ 7.4, $^4J(H^{12}H^{14})$ 1.7, H^{14}], 7.19 [d, $^3J(H^2H^3)$ 2.4, H^3], 7.00 [dd, $^3J(H^{12}H^{13})$ 7.6, H^{12}], 6.91 [dd, $^4J(H^{13}H^{15})$ 0.5, H^{15}], 6.78 (dt, H^{13}), 6.03 (dd, H^2), 4.54 [dt, $^3J(H^4H^9) = {}^3J(H^4H^5_{eq})$ 3.5, $^3J(H^4H^5_{ax})$ 12.9, H^4], 3.95 [br, $^3J(H^8_{ax}H^9) = {}^3J(H^8_{eq}H^9)$ 2–3 Hz, H^9] and 2.25–1.50 (8 H, 6m, CH_2); δ_C(100.25 MHz, 25 °C, $CDCl_3$) 165.4 (C^{10}), 161.1 (C^{16}), 139.0 (C^1), 132.4 (C^{12}), 131.5 (C^{14}), 127.0 (C^3), 118.7, 118.6 (C^{11}, C^{15}), 116.8 (C^{13}), 104.7 (C^2), 68.4 (C^4), 63.8 (C^9), 32.1 (C^5), 26.1, 25.5 (C^8, C^6) and 20.2 (C^7); *m/z* (EI) 269 (3, M^+), 201 (3, $M - C_3H_4N_2$), 120 (9, C_7H_6NO), 81 (11, $C_3H_3N_2$–CH_2), 69 (100, $C_3H_5N_2$) and 41 (19%, C_3H_5).

***rac*-2,4-Dichloro-6-[*cis*-(2-pyrazol-1-yl)cyclohexyliminomethyl]phenol Vb.** (Found: C, 56.25; H, 5.15; Cl, 20.8; N, 12.45. $C_{16}H_{17}Cl_2N_3O$ requires C, 56.8; H, 5.05; Cl, 20.95; N, 12.4%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3406 (br) (OH), 1628vs (C=N); δ_H(400.13 MHz, 25 °C, $CDCl_3$) 14.69 (s, OH), 7.48 (s, H^{10}), 7.47 [d, $^4J(H^{12}H^{14})$ 2.5, H^{12}], 7.35 [d, $^3J(H^1H^2)$ 2.5, H^1], 7.19 [d, $^3J(H^2H^3)$ 2.0, H^3], 6.87 (d, H^{14}), 6.06 (dd, H^2), 4.53 [dt, $^3J(H^4H^9) = {}^3J(H^4H^5_{eq})$ 3.5, $^3J(H^4H^5_{ax})$ 12.6, H^4], 4.08 [br, $^3J(H^8_{ax}H^9) = {}^3J(H^8_{eq}H^9)$ *ca.* 2–3 Hz, H^9] and 2.25–1.50 (8 H, 6m, CH_2); δ_C(100.25 MHz, 25 °C, $CDCl_3$) 163.9 (C^{10}), 157.3 (C^{16}), 139.4 (C^1), 132.4 (C^{14}), 129.0 (C^{12}), 127.0 (C^3), 122.9, 122.4 (C^{11}, C^{15}), 119.1 (C^{13}), 104.7 (C^2), 67.7 (C^4), 63.3 (C^9), 31.4 (C^5), 25.7, 25.5 (C^8, C^6) and 20.1 (C^7); *m/z* [chemical ionisation (CI), ^{35}Cl] 338 (100, $M + H$), 337 (50, M^+) and 269 (3%, $M - C_3H_4N_2$).

***rac*-*cis*-2-[2-(Pyrazol-1-yl)cyclohexyliminomethyl]pyridine Vc.** $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1647vs (C=N); δ_H(400.13 MHz, 25 °C, $CDCl_3$) 8.43 [d, $^3J(H^{14}H^{15})$ 5.0, H^{15}], 7.88 [d, $^3J(H^{12}H^{13})$ 7.5, H^{12}], 7.67 (s, H^{10}), 7.66 [d, $^3J(H^2H^3)$ 2.0, H^3], 7.58 [t, $^3J(H^{13}H^{14})$ 7.5, H^{13}], 7.31 [s, $^3J(H^1H^2) < 1.0$, H^1], 7.13 (dd, H^{14}), 5.91 (br, H^2), 4.45 [dt, $^3J(H^4H^9) = {}^3J(H^4H^5_{eq})$ 3.5, $^3J(H^4H^5_{ax})$ 12.5, H^4], 3.85 [br, $^3J(H^8_{ax}H^9) = {}^3J(H^8_{eq}H^9)$ 2–3 Hz, H^9] and 2.25–1.30 (8 H, 4m, CH_2); δ_C(100.25 MHz, 25 °C, $CDCl_3$) 161.6 (C^{10}), 154.3 (C^{11}), 148.9 (C^{15}), 138.7 (C^1), 136.1 (C^{12}), 126.7 (C^3), 124.3, 120.6 (C^{13}, C^{14}), 104.5 (C^2), 68.6 (C^4), 64.3 (C^9), 29.9 (C^5), 26.8, 25.6 (C^8, C^6) and 19.8 (C^7); *m/z* (EI) 254 (3, M^+), 186 (42, $M - C_3H_4N_2$), 176 (63, $M - C_5H_4N$), 157 (9, C_5H_4N–$CHNC_4H_4$), 145 (52, C_5H_4N–$CHNC_3H_4$), 131 (52, C_5H_4N–$CHNC_2H_2$), 119 (32, C_5H_4N–$CHNCH_2$), 118 (35, C_5H_4N–$CHNCH$), 107 (13, C_5H_4N–$CHNH_2$), 105 (26, C_5H_4N–CNH), 92 (58, C_5H_4N–CH_2), 81 (30, $C_3H_3N_2$–CH_2), 80 (26, C_5H_6N), 79 (41, C_5H_5N), 78 (35, C_5H_4N), 69 (100, $C_3H_5N_2$), 68 (30, $C_3H_4N_2$), 67 (23, $C_3H_3N_2$), 65 (36, C_4H_3N) and 41 (44%, C_3H_5).

***rac*-*cis*-2-[2-(Pyrazol-1-yl)cyclohexyliminomethyl]furan Vd.** (Found: C, 67.65; H, 7.35; N, 16.95. $C_{14}H_{17}N_3O$ requires C, 69.1; H, 7.05; N, 17.25%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1642vs (C=N); δ_H(400.13 MHz, 25 °C, $CDCl_3$) 7.46 [dd, $^3J(H^{13}H^{14})$ 1.2, $^4J(H^{12}H^{14})$ 0.6, H^{14}], 7.43 [d, $^3J(H^1H^2)$ 1.8, H^1], 7.41 (s, H^{10}), 7.28 [d, $^3J(H^2H^3)$ 2.3, H^3], 6.55 [dd, $^3J(H^{12}H^{13})$ 3.4, H^{12}], 6.40 (dd, H^{13}), 6.05 (dd, H^2), 4.52 [dt, $^3J(H^4H^9) = {}^3J(H^4H^5_{eq})$ 3.5, $^3J(H^4H^5_{ax})$ 12.9, H^4], 3.95 [br, $^3J(H^8_{ax}H^9) = {}^3J(H^8_{eq}H^9)$ 2–3 Hz, H^9] and 2.46–1.50 (8 H, 3m, CH_2); δ_C(100.25 MHz, 25 °C, $CDCl_3$) 151.7 (C^{11}), 149.8 (C^{10}), 144.7 (C^{14}), 138.5 (C^1), 127.4 (C^3), 114.2 (C^{12}), 111.4 (C^{13}), 104.4 (C^2), 69.9 (C^4), 64.8 (C^9), 32.9 (C^5), 26.4, 25.9 (C^8, C^6) and 20.1 (C^7); *m/z* (EI) 243 (4, M^+), 175 (10, $M - C_3H_4N_2$), 150 (42, $M - C_4H_3O - CN$), 146 (32, $M - C_3H_4N_2 - C_2H_5$), 134 (8, $M - C_3H_4N_2 - C_3H_5$), 107 (21, C_4H_3O–$CHNCH$), 94 (57, C_4H_3O–CHN), 81 (49, C_5H_5O), 80 (32, $C_4H_4N_2$), 79 (19, $C_4H_3N_2$), 69 (100, $C_3H_5N_2$), 68 (34, $C_3H_4N_2$), 67 (29, $C_3H_3N_2$) and 52 (56%, C_4H_4).

Chloro{*rac*-*cis*-2-[2-(pyrazol-1-yl)cyclohexyliminomethyl]phenolato}palladium(II) 1a. Bis(benzonitrile)dichloropalladium(II) (1.42 g, 3.70 mmol) and triethylamine (0.50 cm^3) were added to a solution of compound **Va** (1.00 g, 3.70 mmol) in dry CH_2Cl_2 (30 cm^3) and the mixture stirred for 48 h at room temperature. The product, which precipitated as a yellow microcrystalline solid, was contaminated with a small amount of triethylammonium chloride and traces of elemental palladium. It can be recrystallised from methanol or concentrated acetonitrile solution at 50 °C, resulting in formation of the acetonitrile adduct **1a**·MeCN as deep orange plates (m.p. 288 °C). Yield 1.27 g (76%) (Found: C, 47.75; H, 4.65; Cl, 7.75; N, 12.35; Pd, 24.0. $C_{16}H_{18}ClN_3OPd\cdot CH_3CN$ requires C, 47.9; H, 4.7; Cl, 7.85; N, 12.4; Pd, 23.6%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1611vs (C=N); δ_H(400.13 MHz, 25 °C, [$^2H_7$]dmf) 8.40 [d, $^3J(H^1H^2)$ 2.0, H^1], 8.38 [d, $^3J(H^2H^3)$ 3.0, H^3], 8.28 (s, H^{10}), 7.42 [dd, $^3J(H^{12}H^{13})$ 8.0, $^4J(H^{12}H^{14})$ 1.8, H^{12}], 7.31 [ddd, $^3J(H^{14}H^{15})$ 8.5, $^3J(H^{13}H^{14})$ 6.8, H^{14}], 6.83 (d, H^{15}), 6.49 (m, H^2, H^{13}), 4.92 [br, $^3J(H^4H^9) = {}^3J(H^4H^5_{eq}) = {}^3J(H^4H^5_{ax})$ 2–3, H^4], 4.10 [dt, $^3J(H^4H^9) = {}^3J(H^8_{eq}H^9)$ 2.0, $^3J(H^8_{ax}H^9)$ 11.6 Hz, H^9] and 2.16–1.22 (8 H, 4m, CH_2); δ_C(100.25 MHz, 25 °C, [$^2H_7$]dmf) 164.1, 162.0 (C^{10}, C^{16}), 145.4 (C^1), 136.0, 135.4, 134.7 (C^3, C^{12}, C^{14}), 120.1 (C^{15}), 118.2 (C^{11}), 115.6 (C^{13}), 107.0 (C^2), 69.0 (C^4), 60.5 (C^9), 28.4, 28.4, 24.4 (C^5, C^6, C^8) and 20.0 (C^7).

Acetato{*rac-cis*-2-[2-(pyrazol-1-yl)cyclohexyliminomethyl]-phenolato}palladium(II) 1b. Compound **Va** (0.20 g, 0.74 mmol) in dry CH_2Cl_2 (5 cm^3) was added dropwise *via* a syringe to a solution of palladium acetate (0.17 g, 0.74 mmol) in dry CH_2Cl_2 (5 cm^3). After 48 h of stirring at room temperature the solvent was removed *in vacuo*. The residue was washed with diethyl ether (20 cm^3) and dried *in vacuo*. Yield 0.27 g (85%), yellow microcrystalline solid (Found: C, 48.55; H, 5.3; N, 10.05. $C_{18}H_{21}N_3O_3Pd$ requires C, 49.85; H, 4.85; N, 9.7%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1610vs (C=N); δ_H(400.13 MHz, 25 °C, CD_2Cl_2) 7.70 [d, $^3J(H^1H^2)$ 2.4, H^1], 7.69 (s, H^{10}), 7.65 [d, $^3J(H^2H^3)$ 2.8, H^3], 7.31 [ddd, $^3J(H^{14}H^{15})$ 8.8, $^3J(H^{13}H^{14})$ 6.8, $^4J(H^{12}H^{14})$ 1.8, H^{14}], 7.18 [dd, $^3J(H^{12}H^{13})$ 7.9, H^{12}], 6.93 (d, H^{15}), 6.57 [ddd, $^4J(H^{13}H^{15})$ 1.0, H^{13}], 6.42 (dd, H^2), 4.75 [br, $^3J(H^4H^9) = {}^3J(H^4H^5_{eq}) = {}^3J(H^4H^5_{ax})$ 2–3, H^4], 3.71 [dt, $^3J(H^4H^9) = {}^3J(H^8_{eq}H^9)$ 2.6, $^3J(H^8_{ax}H^9)$ 12.1 Hz, H^9], 2.12 (s, O_2CCH_3) and 2.54–1.26 (8 H, 4m, CH_2); δ_C(100.25 MHz, 25 °C, CD_2Cl_2) 177.7 (C=O), 164.8 (C^{16}), 162.2 (C^{10}), 142.4 (C^1), 136.0, 134.8 (C^{12}, C^{14}), 132.0 (C^3), 120.2 (C^{15}), 119.6 (C^{11}), 115.6 (C^{13}), 107.2 (C^2), 70.6 (C^4), 60.1 (C^9), 30.1 (CH_3), 28.7 (C^5), 24.7, 24.0 (C^6, C^8) and 19.3 (C^7).

Chloro{*rac-cis*-2-[2-(pyrazol-1-yl)cyclohexyliminomethyl]-pyridine}palladium(II) chloride 2a. The compound [$PdCl_2$-$(PhCN)_2$] (1.11 g, 2.90 mmol) was added to a solution of compound **Vc** (0.74 g, 2.90 mmol) in dry CH_2Cl_2 (30 cm^3). The mixture was stirred for 5 h at room temperature. The solvent was removed *in vacuo* and the brown oily residue recrystallised from CH_2Cl_2–diethyl ether to give bright yellow crystals containing about 2.5 equivalents of CH_2Cl_2 per molecule of complex **2a**. Yield 0.99 g (53%) (Found: C, 32.2; H, 3.4; N, 9.1. $C_{15}H_{18}Cl_2N_4Pd\cdot 2.5CH_2Cl_2$ requires C, 32.65; H, 3.6; N, 8.7%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1624vs (C=N); δ_H(400.13 MHz, −60 °C, CD_2Cl_2), isomer **A**, 10.37 (s, H^{10}), 9.11 [d, $^3J(H^{14}H^{15})$ 4.5, H^{15}], 9.02 [d, $^3J(H^{12}H^{13})$ 7.5, H^{12}], 8.31 [d, $^3J(H^1H^2)$ 2.6, H^1], 8.24 [dd, $^3J(H^{13}H^{14})$ 8.0, H^{13}], 7.96 [d, $^3J(H^2H^3)$ 3.5, H^3], 7.70 (m, H^{14}), 6.55 (dd, H^2), 4.87 [dt, $^3J(H^8_{ax}H^9)$ 12.0, $^3J(H^4H^9) = {}^3J(H^8_{eq}H^9)$ 3.5, H^9], 4.74 [br, $^3J(H^4H^5_{eq}) = {}^3J(H^4H^5_{ax})$ 2–3, H^4) and 2.55–1.30 (8 H, m, CH_2); isomer **B**, 10.52 [d, $^3J(H^9H^{10})$ 2.0, H^{10}], 9.10 [d, $^3J(H^{14}H^{15})$ 4.5, H^{15}], 8.65 [d, $^3J(H^{12}H^{13})$ 7.0, H^{12}], 8.22 [dd, $^3J(H^{13}H^{14})$ 8.0, H^{13}], 8.15 [d, $^3J(H^1H^2)$ 2.0, H^1], 7.95 [d, $^3J(H^2H^3)$ 2.0, H^3], 7.70 (m, H^{14}), 6.44 (t, H^2), 5.00 [dt, $^3J(H^4H^9) = {}^3J(H^4H^5_{eq})$ 3.5, $^3J(H^4H^5_{ax})$ 13.0, H^4], 4.45 [br, $^3J(H^8_{ax}H^9) = {}^3J(H^8_{eq}H^9)$ *ca.* 2–3 Hz, H^9] and 2.55–1.30 (8 H, m, CH_2); isomer ratio **A**:**B** 1.00); *m/z* (FAB, ^{35}Cl, ^{106}Pd) 395 (13, PdLCl) and 359 (2%, $C_{15}H_{17}N_4Pd$).

Dichloro{*rac-cis*-2-[2-(pyrazol-1-yl)cyclohexyliminomethyl]-furan}palladium(II) 2b. The compound [$PdCl_2(PhCN)_2$] (1.57 g, 4.1 mmol) was added to a solution of compound **Vd** (1.0 g, 4.1 mmol) in dry CH_2Cl_2 (30 cm^3). The mixture was stirred for 48 h at room temperature. A brown precipitate formed which was washed three times with CH_2Cl_2 (10 cm^3) and dried *in vacuo*. Yield 1.66 g (96%), orange-brown microcrystalline powder (Found: C, 39.55; H, 3.9; Cl, 17.05; N, 9.85; O, 3.85; Pd, 25.0. $C_{14}H_{17}Cl_2N_3OPd$ requires C, 40.0; H, 4.05; Cl, 16.85; N, 10.0; O, 3.8; Pd, 25.3%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1608vs (C=N).

Bromotricarbonyl{*rac-cis*-2-[2-(pyrazol-1-yl)cyclohexylimino-methyl]phenol}rhenium(I) 3. A solution of [$ReBr(CO)_5$] (0.3 g, 0.74 mmol) and compound **Va** (0.20 g, 0.74 mmol) in thf (20 cm^3) was heated under reflux for 48 h, changing from yellow to orange. After evaporation of the solvent *in vacuo*, the solid residue was washed three times with diethyl ether (10 cm^3) and dried *in vacuo*. Yield: 0.18 g (41%), yellow microcrystalline powder (Found: C, 35.25; H, 3.2; Br, 13.3; N, 6.5; O, 11.25; Re, 31.0. $C_{19}H_{19}BrN_3O_4Re$ requires C, 36.85; H, 3.1; Br, 12.9; N, 6.8; O, 10.35; Re, 30.05%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 2019vs, 1902vs (CO), 1609vs (C=N); (thf) 2020vs, 1914vs, 1888s (CO); δ_H(400.13 MHz, 25 °C, CD_2Cl_2) 10.87 (s, OH), 9.80 (s, H^{10}), 7.88 [d, $^3J(H^1H^2)$ 2.5, H^1], 7.64 [d, $^3J(H^2H^3)$ 2.0, H^3], 7.60 [dd, $^3J(H^{12}H^{13})$ 7.5, $^4J(H^{12}H^{14})$ 1.5, H^{12}], 7.55 [dd, $^3J(H^{14}H^{15})$ 8.8, $^3J(H^{13}H^{14})$ 7.5, H^{14}], 7.04 [ddd, $^4J(H^{13}H^{15})$ 1.1, H^{13}], 6.98 (dd, H^{15}), 6.45 (dd, H^2), 4.62 [dt, $^3J(H^4H^9) = {}^3J(H^4H^5_{eq})$ 3.0, $^3J(H^4H^5_{ax})$ 10.0, H^4], 3.80 [br, $^3J(H^8_{ax}H^9) = {}^3J(H^8_{eq}H^9)$ 2–3 Hz, H^9) and 2.25–1.80 (8 H, 6m, CH_2); δ_C(100.25 MHz, 25 °C, CD_2Cl_2) 196.9 ($2CO_{eq}$), 194.8 (CO_{ax}), not observed (C^{10}, C^{16}), 146.5 (C^1), 137.0 (C^3), 133.8 (C^{12}), 133.2 (C^{14}), 119.9 (C^{15}), 117.4, 117.4 (C^{11}, C^{13}), 107.8 (C^2), 63.0 (C^4, C^9), 33.1 (C^5), 28.7, 23.2 (C^8, C^6) and 20.0 (C^7).

Dichlorooxo{*rac-cis*-2-[2-(pyrazol-1-yl)cyclohexylimino-methyl]phenolato}rhenium(V) 4a and dichloro{*rac-cis*-2,4-dichloro-6-[2-(pyrazol-1-yl)cyclohexyliminomethyl]phenolato}oxo-rhenium(V) 4b. The appropriate compound **Va** or **Vb** (1 mmol) was added to a solution of [NBu_4][$ReOCl_4$] (293 mg, 0.5 mmol) in ethanol (20 cm^3). The resulting brown reaction mixture was heated to reflux for 3 h during which a green precipitate formed, which was filtered off, washed with ethanol and pentane and dried *in vacuo*. Yield 0.20 (73%) of **4a** and 0.20 g (65%) of **4b**, green microcrystalline solids, poorly soluble in organic solvents.

Complex **4a** (Found: C, 35.6; H, 3.65; N, 7.3. $C_{16}H_{18}Cl_2$-N_3O_2Re requires C, 35.5; H, 3.35; N, 7.75%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1614vs (C=N); δ_H[400.13 MHz, 25 °C, $(CD_3)_2SO$], isomer **A**, 8.92 (s, H^{10}), 8.91 [d, $^3J(H^1H^2)$ 2.5, H^1], 8.76 [d, $^3J(H^2H^3)$ 2.5, H^3], 7.69 [ddd, $^3J(H^{14}H^{15})$ 8.5, $^3J(H^{13}H^{14})$ 7.0, $^4J(H^{12}H^{14})$ 1.5, H^{14}], 7.63 [dd, $^3J(H^{12}H^{13})$ 8.0, H^{12}], 7.15 (d, H^{15}), 7.07 (t, H^2), 7.00 (dd, H^{13}), 5.20 [br d, $^3J(H^4H^9) = {}^3J(H^4H^5_{eq})$ *ca.* 2–3, $^3J(H^4H^5_{ax})$ 12.5, H^4], 5.01 [br, $^3J(H^4H^9) = {}^3J(H^8_{eq}H^9) = {}^3J(H^8_{ax}H^9)$ *ca.* 2–3, H^9] and 2.90–1.35 (8 H, 5m, CH_2); isomer **B**, 9.16 (s, H^{10}), 8.98 [d, $^3J(H^1H^2)$ 2.5, H^1], 8.87 [d, $^3J(H^2H^3)$ 2.5, H^3], 7.79 [td, $^3J(H^{14}H^{15}) = {}^3J(H^{13}H^{14})$ 7.8, $^4J(H^{12}H^{14})$ 1.5, H^{14}], 7.75 [dd, $^3J(H^{12}H^{13})$ 8.0, H^{12}], 7.25 (d, H^{15}), 7.13 (t, H^2), 7.10 (dd, H^{13}), 5.17 [br d, $^3J(H^4H^9) = {}^3J(H^4H^5_{eq})$ *ca.* 2–3, $^3J(H^4H^5_{ax})$ 14.0, H^4], 4.77 [br, $^3J(H^4H^9) = {}^3J(H^8_{eq}H^9) = {}^3J(H^8_{ax}H^9)$ *ca.* 2–3 Hz, H^9] and 2.90–1.35 (8 H, 5m, CH_2), isomer ratio **A**:**B** 1.56; δ_C[100.15 MHz, 25 °C, $(CD_3)_2SO$], isomer **A**, 174.7, 174.1 (C^{10}, C^{16}), 147.8 (C^1), 138.5, 138.0, 137.7 (C^3, C^{12}, C^{14}), 121.2, 120.8, 118.8 (C^{11}, C^{13}, C^{15}), 108.7 (C^2), 76.8 (C^4), 60.8 (C^9), 29.7, 28.7, 24.2 (C^5, C^6, C^8), 18.7 (C^7); isomer **B**, 175.8 (C^{10}), 172.0 (C^{16}), 149.2 (C^1), 139.7, 139.0, 138.5 (C^3, C^{12}, C^{14}), 121.5, 120.6 (C^{11}, C^{15}), 120.6 (C^{13}), 109.5 (C^2), 75.4 (C^4), 56.2 (C^9), 29.0, 28.8, 23.9 (C^5, C^6, C^8) and 18.6 (C^7).

Complex **4b** (Found: C, 31.7; H, 2.7; Cl, 22.6; N, 6.95; O, 5.55; Re, 30.1. $C_{16}H_{16}Cl_4N_3O_2Re$ requires C, 31.5; H, 2.65; Cl, 23.25; N, 6.9; O, 5.25; Re, 30.5%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1619vs (C=N); δ_H[400.13 MHz, 25 °C, $(CD_3)_2SO$], isomer **A**, 8.93 [d, $^3J(H^1H^2)$ 2.5, H^1], 8.88 (s, H^{10}), 8.81 [d, $^3J(H^2H^3)$ 2.5, H^3], 8.00 [d, $^4J(H^{12}H^{14})$ 2.5, H^{12}], 7.70 (d, H^{14}), 7.10 (t, H^2), 5.15 [br d, $^3J(H^4H^9) = {}^3J(H^4H^5_{eq})$ *ca.* 2–3, $^3J(H^4H^5_{ax})$ 12.0, H^4], 5.01 [br, $^3J(H^8_{ax}H^9) = {}^3J(H^8_{eq}H^9)$ *ca.* 2–3, H^9] and 2.90–1.35 (8 H, 5m, CH_2); isomer **B**, 9.11 (s, H^{10}), 8.99 [d, $^3J(H^1H^2)$ 2.5, H^1], 8.91 [d,

$^3J(H^2H^3)$ 2.5, H^3], 8.13 [d, $^4J(H^{12}H^{14})$ 2.5, H^{12}], 7.84 (d, H^{14}), 7.15 (t, H^2), 5.12 [br d, $^3J(H^4H^9) = {}^3J(H^4H^5_{eq})$ *ca.* 2–3, $^3J(H^4H^5_{ax})$ 17.6, H^4], 4.78 [br, $^3J(H^8_{ax}H^9) = {}^3J(H^8_{eq}H^9)$ *ca.* 2–3 Hz, H^9] and 2.90–1.35 (8 H, 5m, CH_2); isomer ratio **A**:**B** 1.35.

Crystallography

Intensity data for complex **1a** were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å). The structure was solved by the Patterson method with SHELXS 86[23] and refined (based on F^2) by full-matrix least-squares analysis with SHELXL 93.[24] All non-H atoms were refined with anisotropic thermal parameters. The positions of all H atoms were obtained from the least-squares refinement and were refined with isotropic thermal parameters.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC should quote the full literature citation and the reference number 186/496.

Acknowledgements

The authors thank Professor Dr. W. A. Herrmann, the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support of this work and Dr. E. Herdtweck for X-ray data collection.

References

1 Part 2, C. Thurner, M. Barz, M. Spiegler and W. R. Thiel, *J. Organomet. Chem.*, in the press.
2 (*a*) *Catalytic Asymmetric Synthesis*, ed. E. Ojima, VCH, New York, 1993; (*b*) H. Brunner and W. Zettlmeier, *Handbook of Enantioselective Catalysis with Transition Metal Compounds*, VCH, Weinheim, 1993, vols. I and II; (*c*) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, 1994.
3 K. B. Sharpless, W. Amberg, M. Beller, H. Chen, J. Hartung, Y. Kawanami, D. Lübben, E. Manoury, Y. Ogino, T. Shibata and T. Ukita, *J. Org. Chem.*, 1991, **56**, 4585.
4 L. M. Venanzi and A. Togni, *Angew. Chem.*, 1994, **106**, 517; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 497.
5 M. Barz, E. Herdtweck and W. R. Thiel, *Tetrahedron Asymm.*, 1996, **7**, 1717.
6 M. Barz and W. R. Thiel, unpublished work.
7 M. Calligaris and L. Randaccio, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, London, 1987, vol. 2, pp. 715–738.
8 F. Muth, in *Methoden der Organischen Chemie* (*Houben Weyl*), ed. E. Müller, Georg Thieme Verlag, Stuttgart, 4th edn., 1955, vol. 9, pp. 663–668.
9 A. Hassner, in *Methoden der Organischen Chemie* (*Houben Weyl*), ed. D. Klamann, Georg Thieme Verlag, Stuttgart, 4th edn., 1990, vol. E16a/2, pp. 1255–1265.
10 E. F. V. Scriven and K. Turnbull, *Chem. Rev.*, 1988, **88**, 297.
11 O. Mitsunobu, *Synthesis*, 1981, 1.
12 S. Pawlenko, in *Methoden der Organischen Chemie* (*Houben Weyl*), eds. D. Klamann and H. Hagemann, Georg Thieme Verlag, Stuttgart, 4th edn., 1990, vol. E14b/1, pp. 239–243.
13 U. Burkert and N. C. Allinger, American Chemical Society, Washington, DC, 1982; T. Clark, *A Handbook of Computational Chemistry*, Wiley, New York, 1985; J. W. Ponder and F. M. Richards, *J. Comput. Chem.*, 1987, **8**, 1016.
14 J. E. Anderson, in *The Chemistry of Alkanes and Cycloalkanes*, eds. S. Patai and Z. Rappoport, Wiley, New York, 1992; H.-J. Schneider, R. Price and T. Keller, *Angew. Chem.*, 1971, **83**, 759.
15 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.
16 (*a*) STOE IPDS software manual, version 2.80, 1997; (*b*) E. Prince, *Mathematical Techniques in Crystallography*, Springer, Berlin, 1982.
17 H. Elias, E. Hilms and H. Paulus, *Z. Naturforsch., Teil B*, 1982, **37**, 1266; P. Bandyopadhyay, D. Bandyopadhyay, A. Chakravorty, F. A. Cotton, L. R. Falvello and S. Han, *J. Am. Chem. Soc.*, 1983, **105**, 6327; B. F. Hoskins, C. J. McKenzie and R. Robson, *J. Chem. Soc., Dalton Trans.*, 1992, 3083; M. Kurahashi, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2045.
18 A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27.
19 W. Hieber, R. Schuh and H. Fuchs, *Z. Anorg. Allg. Chem.*, 1941, **248**, 243; S. P. Schmidt, W. C. Trogler and F. Basolo, *Inorg. Synth.*, 1985, **23**, 44.
20 R. E. Cobbledick, L. R. J. Dowdell, F. W. B. Einstein, J. K. Hoyano and L. K. Peterson, *Can. J. Chem.*, 1979, **57**, 2285; W. Tikkanen, W. C. Kaska, S. Moya, T. Layman, R. Kane and C. Krüger, *Inorg. Chim. Acta*, 1983, **76**, L29; M. C. Couldwell and J. Simpson, *J. Chem. Soc., Dalton Trans.*, 1979, 1101; E. W. Abel, V. S. Dimitrov, N. J. Long, K. G. Orrell, A. G. Osborne, H. M. Pain, V. Sik, M. B. Hursthouse and M. A. Mazid, *J. Chem. Soc., Dalton Trans.*, 1993, 597; S. A. Moya, J. Guerrero, R. Pastene, R. Schmidt, R. Sariego, R. Sartori, J. Sanz-Aparicio, I. Fonseca and M. Martinez-Ripoll, *Inorg. Chem.*, 1994, **33**, 2341.
21 G. K. Anderson and M. Lin, *Inorg. Synth.*, 1990, **28**, 61.
22 R. Alberto, R. Schibli, A. Egli, P. A. Schubiger, W. A. Herrmann, G. Artus, U. Abram and T. A. Kaden, *J. Organomet. Chem.*, 1995, **492**, 217.
23 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
24 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Determination, University of Göttingen, 1993.

Received 27*th November* 1996; *Paper* 6/08031F