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cis–trans isomerism and rotational isomerism in triazene-1-oxide bis-chelates of palladium(II)†

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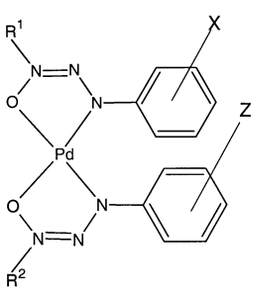
Triazene-1-oxide bis-chelates of palladium(II) reveal the *cis–trans* isomerism. The molecular structures of five *trans* and two *cis* isomers are presented. The *cis* complexes reveal the intramolecular interligand π–π interactions. The intra- and inter-molecular C–H ··· O interactions stabilise the *trans* and *cis* complexes, respectively. The *cis* complexes are usually obtained by thermal isomerisation of the corresponding *trans* complexes in acetonitrile followed by chromatographic separation. The isomerisation occurs only for complexes bearing at least one alkyl substituent in the *ortho* position of the ligand aromatic ring. This phenomenon is interpreted in terms of steric crowding and intermolecular C–H ··· O hydrogen bonding. One- and two-dimensional ^{1}H-NMR studies reveal that Pd(II) triazene-1-oxide *cis*-bis(chelates) bearing at least one ligand with heteromorphically substituted *ortho* positions of the phenyl ring display dynamic rotational isomerism in solution due to rotation of the ligand phenyl ring around the N3–C1 bond. For homoleptic systems this isomerism results in formation of two diastereoisomers: achiral C_s with ligands having opposite axial chirality and a chiral one, C_2, corresponding to those with homomorphic *ortho* groups located on the same or opposite sides of the planar co-ordination core, respectively. For heteroleptic systems either the dynamic racemization of the complex or the diastereoisomeric interconversion is possible depending on whether one or both ligands reveal the axial chirality for non-co-planar conformation. The corresponding processes are observed for the highly sterically congested *trans* complexes.

Non-covalent interactions such as hydrogen bonds, π–π, dipole–dipole and Coulombic interactions and van der Waals forces are crucial for the formation of supramolecular arrays.[1] The formation of inorganic supramolecular systems depends on the latent steric and electronic properties of the single molecular entities. Therefore it is interesting how slight modification of the ligand system affects the geometry of the molecule and its geometry dependent properties. The triazene-1-oxide complexes[2] are thus of particular interest. On the basis of the data available for Ni(II) and Co(II) complexes it has been shown that rather subtle changes in ligand substituents may lead to pronounced changes in their molecular geometry, spin-state, redox behaviour, reactivity and ESR parameters.[2a,3] For cobalt(II) bis-chelates in particular the planar-tetrahedral polytopal isomerism was found to illustrate the strong dependence on ligand substituents of the preferred molecular geometry and spin-state in the solid and solution states.[2a] Results of the early work of Behera and Chakravorty concerning the palladium bis-chelates are noteworthy.[4] The authors showed that for a particular type of ligand substitution, *i.e.* for ligands bearing one *ortho* substituent in the phenyl ring, two separable isomers of palladium bis-chelate were obtained differing in their NMR spectra. The nature of the above isomerism remained unclear until very recently when Chakravorty and co-workers showed it to be due to *cis–trans* isomerism presenting the X-ray structures of complementary pairs of isomers.[5] The following paper stems from our reinvestigation of a series of palladium(II) triazene-1-oxide bis-chelates. Molecular structures of five *trans* bis-chelates have been determined. The *cis–trans* isomerism is possible for any ligand substitution mode involving the *ortho* positions, *i.e.* for unsubstituted *ortho* positions, with an alkyl substituent present in one or both *ortho* positions. Conversely, the thermal *trans–cis* isomerisation in acetonitrile solution does not occur for complexes containing aromatic rings bearing no substituent in an *ortho* position. Molecular structures of two *cis* bis-chelates have been determined. The ability of *trans* complexes to undergo thermal isomerisation to *cis* ones was found to be dependent on intramolecular C–H ··· O hydrogen bonding correlating with the ligand phenyl substitution mode. NMR studies revealed the dynamic rotational isomerism in *cis* complexes of the ligands bearing the heteromorphically substitued *ortho* positions of the phenyl ring. Different patterns of rotamer interconversions were found, depending on the ligands, in homoleptic and heterolepetic bis-chelates involving racemization and diastereomeric interconversion.



$Pd(OR^1N_3C_6H_{5-n}X_n)(OR^2N_3C_6H_{5-n}Z_n)$ *cis*- or *trans*

R^1, R^2 = Me, Et, Pr^i,Bu^t

X, Z = H, 2-Me, 4-Me, 2,4-Me, 2,3-Me, 2,5-Me, 2,6-Me, 2-Bu^t,2-Me-6-Et

† Electronic supplementary information (ESI) available: NMR spectra. See http://www.rsc.org/suppdata/dt/b1/b106652h/

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Table 1 Crystallographic data for complexes **1**, **2**, **3**, **4**, **5**, **6** and **7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_{22}H_{32}N_6O_2Pd$	$C_{20}H_{28}N_6O_2Pd$	$C_{24}H_{36}N_6O_2Pd$	$C_{22}H_{32}N_6O_2Pd$	$C_{18}H_{28}N_6O_2Pd$	$C_{16}H_{20}N_6O_2Pd$	$C_{18}H_{24}N_6O_2Pd$
M	518.94	490.88	546.99	518.94	466.86	434.78	462.83
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	28.306(8)	8.254(1)	8.785(1)	14.138(3)	10.307(2)	8.223(2)	9.098(2)
b/Å	5.995(1)	11.666(2)	16.359(2)	9.568(2)	7.982(2)	8.536(2)	9.918(2)
c/Å	17.074(4)	12.134(2)	9.334(1)	17.685(4)	13.628(3)	14.290(3)	13.036(3)
α/°	—	—	—	—	—	103.96(3)	88.08(3)
β/°	122.72(3)	98.62(1)	98.55(1)	94.49(3)	97.12(3)	95.80(3)	74.01(3)
γ/°	—	—	—	—	—	107.42(3)	65.39(3)
V/Å^3	2437.6(10)	1155.2(3)	1326.5(3)	2385.0(9)	1112.5(4)	912.4(4)	1023.6(4)
Z	4	2	2	2	2	2	2
μ/mm^{-1}	0.790	0.829	0.730	0.808	0.857	1.039	0.931
T/K	293(1)	293(1)	293(1)	293(1)	293(10)	293(1)	293(1)
$R1$	0.0324	0.0249	0.0500	0.0196	0.0436	0.0211	0.0660
$wR2$ (F^2, all data)	0.1062	0.0699	0.1689	0.0456	0.1138	0.0573	0.1772
Measured/Independent reflections/R_{int}	1651/1580/ 0.0145	2188/2029/ 0.0231	2480/2336/ 0.0129	2683/2557/ 0.0143	7074/2708/ 0.0203	3458/3215/ 0.0432	7009/4659/ 0.0441

Experimental

Materials and methods

All ligands apart from those bearing *ortho tert*-butyl groups were obtained as described previously.[2a] Dichloromethane and hexane were purified according to standard methods.[6] Reagent grade acetonitrile and acetone were used without further purification. Palladium acetate was prepared as described in ref. 7. Mass spectra were measured using a Finnigan Mat TSQ 700 mass spectrometer using an ESI ionisation source in chloroform–methanol solutions.

UV VIS spectra were measured with a Cary 5 spectrometer. Column chromatography was performed on silica gel (60–120 mesh). Thin layer chromatography (TLC) was performed with the use of Merck silica gel plates.

NMR spectroscopy

Both 1D and 2D NMR spectra were measured on a Bruker AMX 300 spectrometer operating in the quadrature detection mode at 300 MHz. The positions of resonances were referenced to the residual solvent peak and recalibrated to Me_4Si. Magnitude standard COSY-90 and magnitude and phase-sensitive NOESY spectra were acquired. The 2D spectra were collected by using 1024 data points in t_2 over the desired bandwidth with 1024 blocks and 32 scans per block, in which 4 dummy scans were included. The repetition time was 2 s in both experiments, the mixing time was 0.6 s for NOESY experiments. Prior to Fourier transformation and symmetrization the 2D matrix in each dimension was multiplied with a 30° shifted sine-bell squared window function and processed to obtain a 1024 t_2 × 1024 t_1 word square-matrix. The NOESY spectra were processed in the phase-sensitive or magnitude modes.

X-Ray crystallography

Crystal data for *trans*-**1**–**5** and *cis*-**6**–**7** complexes are summarised in Table 1. All crystals were grown from dichloromethane apart from *trans*-**5** which was grown from hot MeCN. All measurements for **1**–**4** and **6** were performed on a Kuma KM4 diffractometer with graphite-monochromated Mo-Kα radiation and a scintillation counter. Data for *trans*-**5** and **7** were collected on a Kuma KM4CCD diffractometer with graphite-monochromated Mo-Kα radiation. The structures were solved by conventional heavy-atom methods using the SHELXS86 program[8] and refined by the full-matrix least-squares methods on all F^2 data using the SHELXL93 or SHELXL97 programs.[9,10] Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atom or from the $\Delta\rho$ maps and refined with isotropic thermal parameters as independent atoms. In **2** the Bu^t groups are disordered with two positions (3 : 1) rotated around the N–C bond from each other by 60°. The C atoms with an occupancy factor of 0.25 were refined with isotropic thermal parameters. The hydrogen atoms for this orientation were not located.

CCDC reference numbers 153406, 153407, 153413–153415, 178675 and 178676.

See http://www.rsc.org/suppdata/dt/b1/b106652h/ for crystallographic data in CIF or other electronic format.

Synthesis of ($OMeN_3C_6H_4Bu^t$-2)H and ($OPr^iN_3C_6H_4Bu^t$-2)H ligands

The ligands were prepared by coupling the diazotised (at temperatures below −10 °C) *ortho*-*tert*-butylaniline with appropriate *N*-alkylhydroxylamine following the procedure described earlier.[2a] The oily products obtained were extracted with hexane, dried over magnesium sulfate, boiled with charcoal and the solvent removed on a rotary evaporator. The products were chromatographed on silica gel using dichloromethane and dichloromethane–hexane (2 : 1) as eluents for ($OMeN_3C_6H_4Bu^t$-2)H and ($OPr^iN_3C_6H_4Bu^t$-2)H, respectively. The first two mobile yellow fractions were discarded. The less mobile, brown fraction was then eluted with acetone. Evaporation of the solvent yielded brown, semi-oily products. The former ligand was characterised by its NMR spectra.[11] The latter, bearing the *N*-isopropyl group decomposes rapidly and was therefore used for synthesis immediately after chromatography.

Synthesis of complexes

In a typical synthesis of homoleptic bis-chelates 140 mg of palladium acetate (0.625 mmol) was dissolved in 15 ml of acetone, filtered and subsequently added dropwise to a boiling solution of 1.25 mmol of the ligand in 10 ml of acetone. The solution was kept under reflux for about 30 minutes and left overnight. The separated red to pink–violet product was filtered off, washed with cold methanol and dried in air. The alternative method involved the removal of the solvent followed by column chromatography. Using these methods only *trans* isomers were isolated.

Formation of *cis* isomers

The *trans* complex was dissolved in acetonitrile (usually about 10 ml of the solvent was taken for each 10 mg of the complex)

and the solution was refluxed for a few days. The isomerisation was monitored by means of TLC (in each case the R_f's of *cis* isomers were smaller than those of the *trans* isomers). The isomerisation was usually accompanied by a partial demetallation and formation of an immobile yellow species. The acetonitrile was removed on a rotary evaporator and the resulting sample was chromatographed on silica gel with an appropriate eluent. It was found that extensive heating should be avoided, as this may lead to a partial conversion to *trans* complexes. The yield of the *cis* complex of bis-chelates obtained was dependent on the ligand system and varied from about 50% for $Pd(OEtN_3C_6H_3Me\text{-}2,3)_2$ to about 15% for $Pd(OMeN_3C_6H_4Me\text{-}2)_2$. The heteroleptic *cis*-complexes were additionally characterized by their mass spectra.

$Pd(OBu^tN_3C_6H_4Me\text{-}4)_2$ (1). For this complex, (bearing no methyl groups in the *ortho* position of the phenyl ring) the procedure involving heating of the *trans* complex in acetonitrile did not result in formation of the *cis* isomer. Therefore the following procedure was applied: the reaction mixture of the ligand and palladium(II) acetate in 25 ml of boiling acetone, (which revealed the presence of both isomers in the TLC), was rapidly poured into 400 ml of a water–ice mixture. The resulting pink precipitate containing both isomers was filtered, dried on air and chromatographed using dichloromethane as eluent ($R_f^{trans} = 0.95$, $R_f^{cis} = 0.73$).

trans isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28–7.02 (dd, J = 7.8 Hz, 8H, aromatic), 2.29 (s, 6H, 4-*Me*), 1.54 (s, 18H, C*Me*$_3$). (Calc. for $PdC_{22}H_{32}N_6O_2$: C, 50.92; H, 6.22; N, 16.19. Found C, 50.80; H, 6.25; N, 16.10%).

cis isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.52 (AB spectrum, 8H, aromatic), 2.14 (s, 6H, 4-*Me*), 1.53 (s, 18H, C*Me*$_3$). (Calc. for $PdC_{22}H_{32}N_6O_2$: C, 50.92; H, 6.22; N, 16.19. Found C, 50.91; H, 6.04; N, 16.34%).

$Pd(OBu^tN_3C_6H_5)_2$ (2). Only the *trans* isomer was isolated. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (dd, 2H), 7.24 (dd, 4H), 7.00 (dd, 4H, aromatic), 1.57 (18H, C*Me*$_3$). (Calc. for $PdC_{20}H_{28}N_6O_2$: C, 48.96; H, 5.75; N, 17.11. Found C, 48.94; H, 5.66; N, 17.22%).

$Pd(OBu^tN_3C_6H_3Me\text{-}2,3)_2$ (3). The separation was performed using dichloromethane as eluent ($R_f^{trans} = 0.76$, $R_f^{cis} = 0.65$).

trans isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11–6.93 (br m, 6H, aromatic), 1.41 (s, 18H, ^{t}C*Me*$_3$), 2.28, 2.27 (s, 6H, s, 6H, 2-*Me*, 3-*Me*). (Calc. for $PdC_{24}H_{36}N_6O_2$: C, 52.50; H, 6.63; N, 15.36. Found C, 52.55; H, 6.70; N, 15.33%).

cis isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.66–6.47 (br m, 6H, aromatic), 1.49 (s, 18H, ^{t}C*Me*$_3$), 1.96, 1.92 (s, 6H, s, 6H, 2-*Me*, 3-*Me*). (Calc. for $PdC_{24}H_{36}N_6O_2$: C, 52.50; H, 6.63; N, 15.36. Found C, 52.68; H, 6.56; N, 15.25%).

$Pd(OMeN_3C_6H_4Bu^t\text{-}2)_2$ (4). *cis* and *trans* isomers were separated chromatographically using dichloromethane as eluent ($R_f^{trans} = 0.76$, $R_f^{cis} = 0.31$).

trans isomer. ^{1}H NMR (294 K, $CDCl_3$): δ 7.43–7.17 (overlapping multiplets, 8H, aromatic), 3.54 (s, 6H, N*Me*), 1.50 (s, 18H, C*Me*$_3$). (Calc. for $PdC_{22}H_{32}N_6O_2$: C, 50.92; H, 6.22, N, 16.19. Found C, 51.10; H, 6.35; N, 15.90%).

cis isomer. ^{1}H NMR (294, d_8-toluene): δ 7.29 (d, 2H, 3-*H*), 6.97 (dd, 2H, 4-*H*), 6.75 (br d, 2H, 6-*H*), 6.50 (br t, 2H, 5-*H*), 3.28 (6H, s, N*Me*), 1.22 (br s, 18H, C*Me*$_3$). (Calc. for $PdC_{22}H_{32}N_6O_2$: C, 50.92; H, 6.22; N, 16.19. Found C, 51.12; H, 6.50; N, 15.85%).

$Pd(OMeN_3C_6H_3Me\text{-}2,Et\text{-}6)_2$ (5). The separation was performed using CH_2Cl_2 as eluent. ($R_f^{trans} = 0.87$, $R_f^{cis} = 0.27$).

trans isomer. ^{1}H NMR (295 K, $CDCl_3$): δ 1.25 (t, J = 7.5 Hz, 3H, CH_2CH_3), 1.26 (t, J = 7.6 Hz, 3H, $[CH_2CH_3]'$), 2.38 (s, 6H, 2-CH_3 + 2-$[CH_3]'$), 2.7–2.94 (m, 4H, 2-CH_2CH_3 + 2-$[CH_2CH_3]'$), 3.54 (s, 6H, NCH_3 + $[NCH_3]'$), 7.02–7.14 (m, 6H, aromatics). (Calc. for $PdC_{20}H_{28}N_6O_2$: C, 48.94; H, 5.75; N, 17.11. Found C, 48.87; H, 567; N, 17.04%).

cis isomer. ^{1}H NMR (300 K, d_8-toluene): δ 1.03 (t, J = 7.6 Hz, 3H, CH_2CH_3), 1.07 (t, J = 7.6Hz, 3H, $[CH_2CH_3]'$), 2.10 (s, 3H, 2-CH_3), 2.12 (s, 3H, 2-$[CH_3]'$), 2.22 and 2.87 (m, 2H, CH_2), 3.10 (s, 6H, NCH_3 + $[NCH_3]'$), 6.39 (d, 1H, J = 7.4 Hz), 6.47 (d, 1H, J = 7.4 Hz), 6.49 (d, 1H, J = 7.6 Hz), 6.56 (d, 1H, J = 6.0 Hz), 6.77 (t, 2H, J = 7.53 Hz). (Calc. for $PdC_{20}H_{28}N_6O_2$: C, 48.94; H, 5.75; N, 17.11. Found C, 49.06; H, 5.77; N, 17.14%).

$Pd(OMeN_3C_6H_4Me\text{-}2)_2$ (6). The separation was performed using dichloromethane as eluent ($R_f^{trans} = 0.60$, $R_f^{cis} = 0.12$).

trans isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16–7.09 (m, 8H, aromatic), 3.63 (s, 6H, N*Me*), 2.40 (s, 6H, 2-*Me*). UV-VIS ($CHCl_3$): 530 (250), 345 (14400), 260 nm (21400 dm^3 cm^{-1} mol^{-1}). (Calc. for $PdC_{16}H_{20}N_6O_2$: C, 44.20; H, 4.64; N, 19.32. Found C, 44.06; H, 4.71; N, 19.42%).

cis isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.80–6.56 (m, 8H, aromatic), 3.72 (s, 6H, N*Me*), 2.40 (s, 6H, 2-*Me*). UV-VIS ($CHCl_3$): 540 (140), 340 (10100), 250 nm (15800 dm^3 cm^{-1} mol^{-1}). (Calc. for $PdC_{16}H_{20}N_6O_2$: C, 44.20; H, 4.64; N, 19.32. Found C, 44.41; H, 4.64; N, 19.25%).

$Pd(OMeN_3C_6H_3Me\text{-}2,4)_2$ (7). *cis* and *trans* isomers were separated using dichloromethane as eluent ($R_f^{trans} = 0.75$, $R_f^{cis} = 0.28$).

trans isomer. ^{1}H NMR (294 K, $CDCl_3$): δ 7.24–6.94 (m, 6H, aromatic), 3.62 (s, 6H, N*Me*), 2.36, 2.15 (s, 6H, s, 6H, 2-*Me* + 4-*Me*). (Calc. for $PdC_{18}H_{24}N_6O_2$: C, 46.71; H, 5.23; N, 18.15. Found C, 46.85; H, 5.20; N, 18.10%).

cis isomer. ^{1}H NMR (294 K, d_8-toluene): δ 6.61 (d, 2H, J = 7.9 Hz, 6-H), 6.37 (br d, 2H, 5-H), 6.28 (br s, 2H, 3-H), 3.07 (s, 6H, N*Me*), 2.12, 2.03 (s, 6H, s, 6H, 2-*Me* + 4-*Me*). (Calc. for $PdC_{18}H_{24}N_6O_2$: C, 46.71; H, 5.23; N, 18.15. Found C, 46.70; H, 5.25; N, 18.20%).

$Pd(OPr^iN_3C_6H_4Me\text{-}2)_2$ (8). The separation was performed using dichloromethane as eluent ($R_f^{trans} = 0.75$, $R_f^{cis} = 0.48$).

trans isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24–7.06 (m, 8H, aromatic), 4.20 (septet, 2H, C*H*Me$_2$, J = 6.7 Hz), 1.36 (d, 12H, CH*Me*$_2$), 2.39 (s, 6H, 2-*Me*). (Calc. for $PdC_{20}H_{28}N_6O_2$: C, 48.96; H, 5.75; N, 17.12. Found C, 48.80; H, 5.71; N, 17.02%).

cis isomer. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.80–6.48 (m, 8H, aromatic), 4.33 (septet, 2H, C*H*Me$_2$, J = 6.7 Hz), δ = 1.40 (d, 12H, CH*Me*$_2$), 2.11 (s, 6H, 2-*Me*). (Calc. for $PdC_{20}H_{28}N_6O_2$: C, 48.96; H, 5.75; N, 17.11. Found C, 48.90; H, 5.73; N, 16.92%).

$Pd(OEtN_3C_6H_3Me\text{-}2,3)_2$ (9). The separation was performed using dichloromethane as eluent ($R_f^{trans} = 0.75$, $R_f^{cis} = 0.40$).

trans isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.05–6.99 (m, 6H, aromatic), 3.88 (q, 4H, J = 7.2 Hz, NCH_2Me), 1.34 (t, 6H, NCH_2CH_3), 2.31, 2.27 (s, 6H, s, 6H, 2-*Me*, 3-*Me*). (Calc. for $PdC_{20}H_{28}N_6O_2$: C, 48.96; H, 5.75; N, 17.11. Found C, 48.84; H, 5.78; N, 16.98%).

cis isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.68–6.54 (br m, 6H, aromatic), 3.97 (q, 4H, J = 7.2 Hz, NCH_2Me), 1.43 (t, 6H, NCH_2CH_3), 1.93 (s, 12H, 2-*Me*, 3-*Me*). (Calc. for $PdC_{20}H_{28}N_6O_2$: C, 48.96; H, 5.75; N, 17.11. Found C, 49.01; H, 5.75; N, 17.05%).

$Pd(OMeN_3C_6H_3Me\text{-}2,5)_2$ (10). The separation was performed using dichloromethane–hexane (3 : 1) as eluent ($R_f^{trans} = 0.5$, $R_f^{cis} = 0.1$).

trans isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.03–6.87 (m, 6H, aromatic), 3.63 (s, 6H, N*Me*), 2.37, 2.29 (s, 6H, s, 6H, 2-*Me*, 5-*Me*). (Calc. for $PdC_{18}H_{24}N_6O_2$: C, 46.71; H, 5.23; N, 18.15. Found C, 46.70; H, 5.24; N, 18.09%).

cis isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.34 (s, 2H, 6-*H*), 6.57 (AB spectrum, 4H, 3-*H*, 4-*H*), 3.71 (s, 6H, N*Me*), 2.04,

1.98 (s, 6H, s, 6H, 2-*Me*, 5-*Me*). (Calc. for $PdC_{18}H_{24}N_6O_2$: C, 46.71; H, 5.23; N, 18.15. Found C, 46.75; H, 5.27; N, 17.90%).

Pd(OPr^{i}N$_3$C$_6$H$_4$Bu^t-2)$_2$ (11). *cis* and *trans* isomers were separated using dichloromethane–hexane (2 : 1) as eluent (R_f^{trans} = 0.72, R_f^{cis} = 0.64).

trans isomer. ^{1}H NMR (294 K, $CDCl_3$): δ 7.42–7.14 (overlapping multiplets, 8H, aromatic), 4.07 (septet, 2H, J = 6.8 Hz, C*H*Me$_2$), 1.50 (s, 18H, C*Me*$_3$), 1.22 (d, 12H, CH*Me*$_2$). (Calc. for $PdC_{26}H_{40}N_6O_2$: C, 54.31; H, 7.01; N, 14.61. Found C, 54.47; H, 7.15; N, 14.73%).

cis isomer. ^{1}H NMR (294 K, d$_8$-toluene): δ 7.10 (d, 2H, 3-*H*), 6.76 (dd, 2H, 4-*H*), 6.57 (d, 2H, J = 7.7 Hz, 6-*H*), 6.27 (t, 2H, 5-*H*), 3.99 (septet, J = 6.6 Hz, 2H, C*H*Me$_2$), 1.51 (s, 18H, C*Me*$_3$), 1.14 (d, 6H, CH*Me*$_2$). (Calc. for $PdC_{26}H_{40}N_6O_2$: C, 54.31; H, 7.01; N, 14.61. Found C, 54.55; H, 7.25; N, 14.80%).

Pd(OPr^{i}N$_3$C$_6$H$_3$Me-2,6)$_2$ (12). *cis* and *trans* isomers were separated using dichloromethane as eluent (R_f^{trans} = 0.80, R_f^{cis} = 0.70).

trans isomer. ^{1}H NMR (294 K, $CDCl_3$): δ 7.01 (s, 6H, aromatic), 4.10 (septet, 2H, C*H*Me$_2$), 2.38 (s, 12H, 2,6-*Me*), 1.28 (d, J = 6.6 Hz, CH*Me*$_2$). (Calc. for $PdC_{22}H_{32}N_6O_2$: C, 50.92; H, 6.22; N, 16.19. Found C, 50.81; H, 6.15; N, 16.33%).

cis isomer. ^{1}H NMR (294 K, $CDCl_3$): δ 6.73 (t, 2H, J = 7.3 Hz, 4-H), 6.50 (d, 4H, 3-H, 5-H), 4.32 (septet, 2H, J = 6.6 Hz, C*H*Me$_2$), 2.01 (s, 12H, 2,6-*Me*), 1.40 (d, 12H, CH*Me*$_2$). (Calc. for $PdC_{22}H_{32}N_6O_2$: C, 50.92; H, 6.22; N, 16.19. Found C, 51.05; H, 6.34; N, 15.94%).

Pd(OPr^{i}N$_3$C$_6$H$_4$Me-2)(OMeN$_3$C$_6$H$_4$Me-2) (13). This heteroleptic complex was obtained by reaction of stoichiometric amounts of palladium acetate and both ligands (1 : 1 : 1) in acetone. TLC of the reaction mixture showed the presence of approximately equal amounts of *trans* isomers of homoleptic parent bis-chelates and the mixed-ligand heteroleptic complex. The R_f value for the latter was intermediate between those of the homoleptic bis-chelates (R_f^{trans} = 0.70, dichloromethane). Upon removal of the solvent the *trans* isomer of the heteroleptic complex was isolated by means of column chromatography (dichloromethane). Its isomerisation in acetonitrile resulted in formation of the heteroleptic *cis* isomer and residual amounts of parent bis-chelate *trans* isomers. The *cis* isomer was isolated by column chromatography using dichloromethane as eluent (R_f = 0.2).

trans isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.2–7.0 (m, 8H, aromatic), 4.18 (septet, 1H, C*H*Me$_2$′), 3.65 (s, 3H, N*Me*), 2.42, 2.37 (s, 3H, s, 3H, 2*Me* + 2*Me*′), 1.34 (d, J = 6.6 Hz, 6H, CH*Me*$_2$). (Calc. for $PdC_{18}H_{24}N_6O_2$: C, 46.71; H, 5.23; N, 18.15. Found C, 46.65; H, 5.27; N, 18.11%).

cis isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.8–6.5 (m, 8H, aromatic), 4.35 (septet, 1H, J = 6.7 Hz, NC*H*Me$_2$), 1.41 (d, 6H, NCH*Me*$_2$), 3.73 (s, 3H, N*Me*), 2.05, 2.02 (s, 3H, s, 3H, 2-*Me* + 2-*Me*′). (Calc. for $PdC_{18}H_{24}N_6O_2$: C, 46.71; H, 5.23; N, 18.15. Found C, 46.90; H, 5.20; N, 18.18%).

Pd(OPr^{i}N$_3$C$_6$H$_3$Me-2,6)(OMeN$_3$C$_6$H$_4$Cl-4) (14). Palladium acetate and the corresponding ligands in 1 : 1 : 1 ratio (0.625 mmol each) were reacted in boiling acetone (30 ml) for 30 minutes. Upon cooling to 20 °C a grey–violet precipitate was deposited which contained mainly the parent bis-chelate of the chloro-substituted ligand. The solution was filtered off and kept overnight at −15 °C yielding violet crystals of *trans*-**12**. The solution was filtered off and acetone removed on a rotary evaporator. The resulting solid containing mainly the *trans* isomer of heteroleptic bis-chelates was separated from residual amounts of parent bis-chelate (the fraction of intermediate mobility) by column chromatography in dichloromethane. (R_f = 0.78). The usual procedure of isomerisation in MeCN yielded the *cis* isomer which was separated by column chromatography (R_f = 0.32, dichloromethane).

trans isomer. ^{1}H NMR (294 K, $CDCl_3$): δ 7.28–7.04 (m, 7H, aromatic), 4.36 (septet, 1H, C*H*Me$_2$), 3.62 (s, 3H, N*Me*), 2.35 (s, 6H, 2-*Me* + 6-*Me*), 1.45 (d, J = 6.6 Hz, 6H, CH*Me*$_2$). (Calc. for $PdC_{18}H_{23}N_6O_2Cl$: C, 43.47; H, 4.66; N, 16.89. Found C, 43.53; H, 4.78; N, 16.69%).

cis isomer. ^{1}H NMR (294 K, d$_8$-toluene): δ 6.90–6.36 (m, 7H, aromatic), 4.35 (septet, J = 6.6 Hz, 1H, C*H*Me$_2$), 3.75 (s, 3H, N*Me*), 2.06 (s, 6H, 2-*Me* + 6-*Me*), 1.41 (d, 6H, CH*Me*$_2$). (Calc. for $PdC_{18}H_{23}N_6O_2Cl$: C, 43.47; H, 4.66; N, 16.89. Found C, 43.60; H, 4.80; N, 16.70%). MS, *m*/*z* 497 (M^+).

Pd(OMeN$_3$C$_6$H$_3$Me-2,4)(OPr^{i}N$_3$C$_6$H$_4$Cl-4) (15). Palladium acetate and the corresponding ligands in a 1 : 1 : 1 ratio (0.625 mmol each) were reacted in boiling acetone (30 ml) for 30 minutes. Upon cooling to −15 °C a mixture of all three *trans* isomers deposited and were filtered off. The amount of heteroleptic bis-chelate was, however, appreciably higher in solution, as shown by TLC. The solvent was removed and the *trans* isomer of mixed-ligand heteroleptic bis-chelate was separated by column chromatography using dichloromethane–hexane (2 : 1) as eluent. The heteroleptic complex was eluted as a fraction of intermediate mobility (R_f = 0.67). Isomerisation was performed in MeCN, the *cis* isomer isolated by column chromatography (R_f = 0.27).

trans isomer. ^{1}H NMR (294 K, $CDCl_3$): δ 7.22–6.90 (m, 7H, aromatic), 4.23 (septet, 1H, C*H*Me$_2$), 3.77 (s, 3H, N*Me*), 2.37, 2.27 (s, 3H, s, 3H, 2-*Me* + 4-*Me*), 1.36 (d, J = 6.6 Hz, 6H, CH*Me*$_2$). (Calc. for $PdC_{18}H_{23}N_6O_2Cl$: C, 43.47; H, 4.66; N, 16.89. Found C, 43.63; H, 480; N, 16.64%).

cis isomer. ^{1}H NMR (294 K, d$_8$-toluene): δ 6.68–6.35 (overlapping multiplets, 7H, aromatic), 3.99 (septet, J = 6.7 Hz, 1H, C*H*Me$_2$), 3.07 (s, 3H, N*Me*), 2.17, 2.08 (s, 3H, s, 3H, 2-*Me* + 4-*Me*), 2.11 (d, 6H, CH*Me*$_2$). (Calc. for $PdC_{18}H_{23}N_6O_2Cl$: C, 43.47; H, 4.66; N, 16.89. Found C, 43.43; H, 4.72; N, 16.70%). MS, *m*/*z* 497 (M^+).

Pd(OMeN$_3$C$_6$H$_3$Me-2,4)(OPr^{i}N$_3$C$_6$H$_3$Me-2,6) (16). Palladium acetate and the corresponding ligands in a 1 : 1 : 1 ratio (0.625 mmol each) were reacted in hot acetone (25 ml). After boiling for 30 minutes, the reaction mixture was cooled and the solvent removed. As it was difficult to find a suitable eluent to separate the *trans* isomers the mixture was chromatographed in dichloromethane to separate them from by-products and the *trans* complexes were subsequently heated in acetonitrile. The differences in R_f values of resulting *cis* isomers enabled their separation. Column chromatography with CH_2Cl_2 as eluent resulted in separation of *cis*-**16** (R_f = 0.63). ^{1}H NMR (294 K, d$_8$-toluene): δ 7.05–6.15 (m, 6H, aromatic), 3.98 (septet, J = 6.6 Hz, 1H, C*H*Me$_2$), 3.07 (s, 3H, N*Me*), 2.16, 2.03 [3H, s, 3H, s, 2-Me, 4-Me of (OMeN$_3$C$_6$H$_3$Me-2,4)$^-$], 1.48 [s, 6H, 2,6-Me of (OPr^{i}N$_3$C$_6$H$_3$Me-2,6)$^-$], 1.16 (d, 6H, CH*Me*$_2$). (Calc. for $PdC_{20}H_{28}N_6O_2$: C, 48.94; H, 5.75; N, 17.11. Found C, 49.03; H, 5.97; N, 16.87%). MS, *m*/*z* 491 (M^+).

Pd(OMeN$_3$C$_6$H$_3$Me-2,4)(OEtN$_3$C$_6$H$_3$Me-2,6) (17). The *cis* isomer was isolated by a method analogous to that described for **16** (R_f^{cis} = 0.54, CH_2Cl_2). ^{1}H NMR (294 K, d$_8$-toluene): δ 6.73–6.26 (m, 6H, aromatic), 3.46 (q, 2H, C*H*$_2$CH$_3$), 3.02 (s, 3H, N*Me*), 2.19 [s, 6H, 2,6-*Me* of (OEtN$_3$C$_6$H$_3$Me-2,6)$^-$], 2.14, 2.09 [s, 3H, s, 3H, 2-Me + 4-Me of (OMeN$_3$C$_6$H$_3$Me-2,4)$^-$], 1.01 (t, J = 7.4 Hz, 3H, CH$_2$CH$_3$). (Calc. for $PdC_{19}H_{26}N_6O_2$: C, 47.86; H, 5.50; N, 17.62. Found C, 47.93; H, 5.67; N, 17.77%). MS, *m*/*z* 477 (M^+).

Pd(OMeN$_3$C$_6$H$_4$Bu^t-2)(OPr^{i}N$_3$C$_6$H$_3$Me-2,6) (18). Palladium acetate and the corresponding ligands in a 1 : 1 : 1 ratio (0.625 mmol each) were reacted in hot acetone (25 ml). After boiling for 30 minutes, the reaction mixture was cooled and the solvent removed. The obtained mixture of all three *trans*-bis(chelates)

was first chromatographed using CH_2Cl_2 as eluent. The most mobile *trans*-**12** was separated. The second crop contained the heteroleptic complex and *trans*-**3**. Column chromatography using a dichloromethane–hexane (2 : 1) eluent allowed the separation of this mixture, the heteroleptic complex was isolated as the more mobile fraction.

Isomerization of the *trans* heteroleptic complex in MeCN resulted in formation of its *cis* isomer which was separated from the *trans* one on a column using CH_2Cl_2–hexane (2 : 1) as eluent ($R_f^{trans} = 0.48$, $R_f^{cis} = 0.29$).

trans isomer. ^{1}H NMR (294 K, $CDCl_3$): δ 7.65–7.24 (m, 7H, aromatic), 4.21 (septet, 1H, C*H*Me$_2$), 3.78 (s, 3H, N*Me*), 2.57 (s, 6H, 2,6-*Me*), 1.69 (s, 9H, C*Me*$_3$), 1.44 (d, J = 6.6 Hz, CH*Me*$_2$). (Calc. for $PdC_{22}H_{32}N_6O_2$: C, 50.92; H, 6.22; N, 16.19. Found C, 51.04; H, 6.12; N, 16.03%).

cis isomer. ^{1}H NMR (294 K, d_8-toluene): δ 7.11–6.28 (m, 7H, aromatic), 4.00 (septet, 1H, C*H*Me$_2$), 3.20 (s, 3H, N*Me*), 2.30, 2.10 (br s, 6H, br s, 6H, 2,6-*Me*), 1.45 (s, 9H, C*Me*$_3$), 1.11 (d, J = 6.6 Hz, CH*Me*$_2$). (Calc. for $PdC_{22}H_{32}N_6O_2$: C, 50.92; H, 6.22; N, 16.19. Found C, 51.14; H, 6.34; N, 15.99%). MS, *m*/*z* 519 (M^+).

Pd(OMeN$_3$C$_6$H$_4$Bu^t-2) (OMeN$_3$C$_6$H$_3$Me-2,5) (19). Palladium acetate and the corresponding ligands in a 1 : 1 : 1 ratio (0.625 mmol each) were reacted in hot acetone (30 ml). After boiling for 30 minutes, the reaction mixture was cooled and the solvent removed. The obtained mixture of all three *trans*-bis(chelates) was chromatographed using CH_2Cl_2–hexane (2 : 1) as eluent. The heteroleptic complex was separated as the fraction of intermediate mobility (R_f = 0.58). (In this case some *cis* complexes might be isolated without heating in acetonitrile). The separated *trans*-**19** was heated in MeCN yielding a mixture of *cis*- and *trans* isomers separated by chromatography with CH_2Cl_2 ($R_f^{trans} = 0.67$, $R_f^{cis} = 0.27$).

trans isomer. ^{1}H NMR (294 K, $CDCl_3$): δ 7.3–6.9 (m, 7H, aromatic), 3.62, 3.56 (s, 3H, s, 3H, N*Me* + N*Me*′), 2.38, 2.29 (s, 3H, s, 3H, 2-*Me* + 5-*Me*), 1.50 (s, 9H, C*Me*$_3$). (Calc. for $PdC_{20}H_{28}N_6O_2$: C, 48.94; H, 5.75; N, 17.11. Found C, 48.75; H, 5.98; N, 17.31%).

cis isomer. ^{1}H NMR (294 K, d_8-toluene, dominating species in solution, about 10% of a second set of resonances present, partially overlapping with the dominant set): δ 7.10–6.20 (m, 7H, aromatic), 3.11, 3.06 (s, 3H, s, 3H, N*Me* + N*Me*′), 2.20, 1.86 (s, 3H, s, 3H, 2-*Me* + 5-*Me*), 1.49 (s, 9H, C*Me*$_3$). (Calc. for $PdC_{20}H_{28}N_6O_2$: C, 48.94; H, 5.75; N, 17.11. Found C, 49.09; H, 6.02; N, 16.84%). MS, *m*/*z* 491 (M^+).

Pd(OMeN$_3$C$_6$H$_3$Me-2,4)(OPr^{i}N$_3$C$_6$H$_3$Bu^t-2) (20). The *cis* isomer was isolated as described for **16** ($R_f^{cis} = 0.40$, CH_2Cl_2). This bis-chelate had poor stability and decomposed partially when chromatographed. The NMR spectra of the complex always showed the presence of impurities, presumably the dissociation products. ^{1}H NMR (294 K, d_8-toluene): δ 6.91–6.15 (aromatics), 4.00 (septet, 1H, C*H*Me$_2$), 3.06 (s, 3H, N*Me*), 2.16, 2.03 (s, 3H, s, 3H, 2-Me + 4-Me), 1.49 (s, 9H, CMe$_3$), 1.16 (d, J = 6.7 Hz, 6H, CHMe$_2$). MS, *m*/*z* 519 (M^+).

Results and discussion

Crystal and molecular structures

The structures of five *trans* (**1**–**5**) and two *cis*-bis(chelates) (**6**,**7**) have been determined. Their views and numbering schemes are depicted in Figs. 1 and 2. The molecular structures of *trans*- and *cis*-**6** have been very recently reported independently by Chakravorty and co-workers.[5]

The centrosymmetric molecular geometry of *trans*-bis(chelates) **1**–**3** and **5** is essentially the same as that determined for Pd(OMeN$_3$C$_6$H$_4$Me-4)$_2$.[12] The most pronounced difference between them concerns the twist of the aromatic ring towards the chelate triazene plane.[13] On the other hand **4** is devoid of a symmetry centre with both *tert*-butyl groups located on the same side of the molecular plane. The molecule is slightly distorted from planarity and there is a tetrahedral twist of the

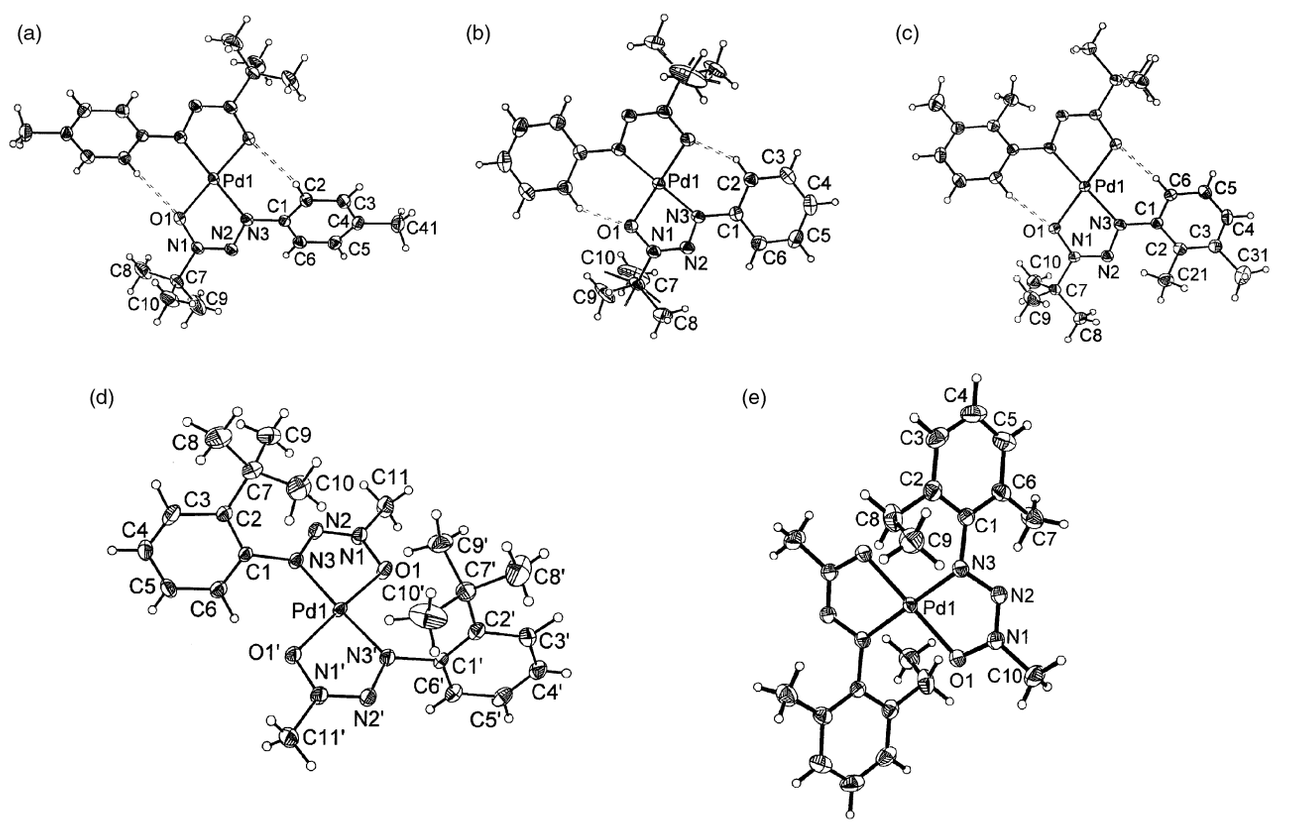

Fig. 1 Representations of the molecular structures of *trans*-Pd(OBu^{t}N$_3$C$_6$H$_4$Me-4)$_2$ (**1**) (a) Pd(OBu^{t}N$_3$C$_6$H$_5$)$_2$ (**2**) (b) Pd(OBu^{t}N$_3$C$_6$H$_3$Me-2,3)$_2$ (**3**) (c) Pd(OMeN$_3$C$_6$H$_4$Bu^t-2)$_2$ (**4**) (d) and Pd(OMeN$_3$C$_6$H$_3$Me-2,Et-6)$_2$ (**5**) (e). The intramolecular C–H ··· O bonds are indicated.

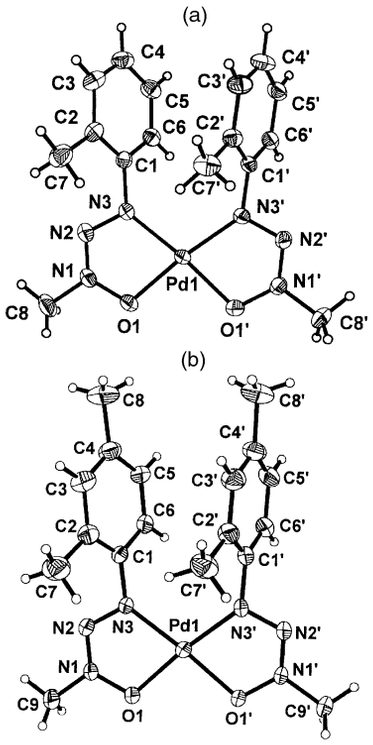

Fig. 2 Representations of the molecular structures of *cis*-Pd(OMeN$_3$-C$_6$H$_4$Me-2)$_2$ (**6**) (a) and Pd(OMeN$_3$C$_6$H$_3$Me-2,4)$_2$ (**7**) (b).

co-ordination core; the angle between best planes Pd–N1–N2–N3–O1 and Pd–N1′–N2′–N3′–O1′ being 6.6(1)°. It is noteworthy that for **5** the molecule present in the crystal is one of two possible *trans* stereoisomers (*vide infra*).

The metal–ligand bond lengths, intraligand bond lengths and angles are identical for *trans* and *cis* complexes. A noteworthy exception is the fairly short N2–N3 distance in the triazene linkage for highly congested *trans*-**4** and **5**.[14] The short N2–N3 bond in **4** is accompanied by directional interactions with hydrogens of the *tert*-butyl group. The distances between the centre of the N2–N3 bond and the H9A and H10A atoms are 2.63 and 2.44 Å, while that between the centre of the N2′–N3′ bond and H10D is 2.36 Å. For *trans*-**5** the hydrogens of the ethyl and methyl groups are placed in the proximity of the N2–N3 bond, the distance between H92 and the centre of the bond being 2.83 Å.

The molecular geometry of the *cis* complexes under study is devoid of a symmetry element, the N_2O_2 co-ordination core is slightly trapezoidally distorted. The planar chelate rings are twisted, resulting in slight tetrahedral distortion of the complex: the angles between Pd1–O1–N1–N2–N3 and Pd1–O1′N1′–N2′–N3′ best planes being 3.4(2)° for both *cis* complexes. The mutual orientation of phenyl rings reveals the interligand π–π interactions. The *ortho* Me groups of both aromatic rings in *cis* complexes are located on the same side of the complex plane. The twist of ligand phenyl rings is 58.72(7) and 65.08(7)° for **6** and 63.4(2) and 70.6(2)° for **7**. Thus, the aromatic rings in *cis* complexes are roughly parallel, their edges bearing methyl substituents being more remote than those bearing hydrogens only. The respective angles between the best planes are 15.3(2) and 14.3(3)° for **6** and **7**, respectively. The distance between centroids of these rings is 3.59 and 3.71 Å, respectively. There is an offset of neighbouring aromatic rings, similar to that characteristic for attractive π–π interactions.[15]

For the systems studied C–H ⋯ O hydrogen bonds[16,17] are present. In the crystals of *trans*-**1**–**3** they are intramolecular and are formed between the C–H groups at *ortho* positions of the aromatic rings and the oxygen atoms of the neighbouring chelate rings on the same molecule (see Fig. 1).

In contrast, in crystals of *cis*-**5** and **6** the C–H ⋯ O interactions are intermolecular. For *cis*-**5** the C–H groups in the *ortho* positions are donors and the ligand oxygen atoms of contiguous molecules are acceptors. For *cis*-**6** the C–H groups in the *meta* position are the donors. These interactions are depicted in Fig. 3. For *cis* complexes the above interactions are

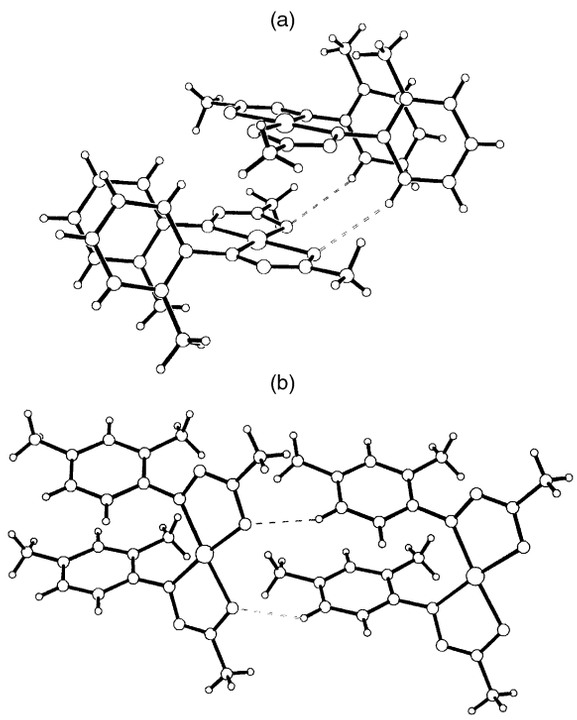

Fig. 3 The intermolecular C–H ⋯ O interactions in *cis*-Pd(OMeN$_3$-C$_6$H$_4$Me-2)$_2$ (**6**) (a) and Pd(OMeN$_3$C$_6$H$_3$Me-2,4)$_2$ (**7**) (b).

crucial for crystal packing, resulting in an infinite polymeric chain within the lattice. The obtained data illustrate the rule that intramolecular hydrogen bonds are stronger than intermolecular ones.[18] The relevant bond distances and angles for both *cis* and *trans* complexes are collected in Table 2.

cis–trans isomerism

The synthesis of the palladium triazene-1-oxide homoleptic bis-chelates is straightforward, involving reaction between the ligand and palladium acetate in acetone. Typically, one isomer deposits on cooling. Monitoring the reaction by TLC shows that two pink–violet isomers are present in solution, the more

Table 2 H-bond lengths (Å) and angles (°)

Compound	D–H ⋯ A	Code	D ⋯ A	H ⋯ A	∠D–H ⋯ A
trans-Pd(OBu^{t}N$_3$C$_6$H$_4$Me-4)$_2$	C(2)–H(2) ⋯ O(1)	$1-x, -y, 1-z$	3.121(6)	2.54(6)	118(4)
trans-Pd(OBu^{t}N$_3$C$_6$H$_5$)$_2$	C(2)–H(2) ⋯ O(1)	$1-x, 1-y, 1-z$	3.036(4)	2.29(4)	135(3)
trans-Pd(OBu^{t}N$_3$C$_6$H$_3$Me-2,3)$_2$	C(6)–H(6) ⋯ O (1)	$1-x, 1-y, 1-z$	3.067(7)	2.49	121
cis-Pd(OMeN$_3$C$_6$H$_4$Me-2)$_2$	C(6)–H(6) ⋯ O(1′)	$-x, 1-y, 1-z$	3.450(4)	2.64(3)	148(2)
cis-Pd(OMeN$_3$C$_6$H$_4$Me-2)$_2$	C(6′)–H(6′) ⋯ O(1)	$-x, 1-y, 1-z$	3.541(4)	2.64(3)	153(2)
cis-Pd(OMeN$_3$C$_6$H$_4$Me-2,4)$_2$	C(5)–H(5) ⋯ O(1)	$-1+x, 1-y, 1-z$	3.501(7)	2.62	159
cis-Pd(OMeN$_3$C$_6$H$_4$Me-2,4)$_2$	C(5′)–H(5′) ⋯ O(1′)	$-1+x, 1-y, 1-z$	3.530(8)	2.70	149

mobile one crystallizing on cooling (*e.g.* **1**–**3**). Heating the solutions of most of the *trans* isomers (with the exception of the isomer bearing no substitutents in the *ortho* position of the phenyl ring) resulted in formation of the second isomer which could be isolated chromatographically. The latter isomers were shown by X-ray methods to be the *cis* isomers. Their NMR spectra exhibit a significant upfield shift of the aromatic protons with all signals occurring below 7.0 ppm. This is indicative of interligand π–π interactions, as observed in the single-crystal X-ray structures.[19]

cis–trans isomerism is a well-recognised feature of palladium(II) complexes, although extensive synthetic efforts have centred on the complexes of monodentate ligands.[20] The data concerning the bis-chelate systems are rather scattered.[21] Triazene-1-oxide Pd(II) bis-chelates seem to be of interest for the following reasons: first, to the best of our knowledge they represent the first case of isolation of both the *cis* and *trans* isomers for bis-chelates exhibiting a PdN_2O_2 co-ordination core. Each isomer is stabilised by another type of weak interaction; the *trans* ones by intramolecular interligand C–H ··· O bonds, the *cis* ones by attractive π–π interactions. The importance of the former type of interaction for the relative population of *cis* and *trans* isomers has been recently demonstrated for palladium alkoxy complexes.[21h] Second, the isolation of both isomers is possible for ligand systems displaying a high degree of steric congestion. Finally, there is a significant correlation between ligand substituents and the ability to undergo *trans–cis* isomerisation. The complexes under study may be divided into two groups, with regard to steric hindrance in the ligand, depending upon whether at least one alkyl substituent is present in the *ortho* position of the phenyl ring (*cf.* ref. 2*a* and 3*e*). The complexes with little steric hindrance (*e.g.* **1** and **2**) show comparable amounts of *trans* and *cis* isomers in the reaction mixture when synthesized in acetone (as seen by TLC) yet their *trans* isomers do not undergo the isomerization in acetonitrile. When synthesized in acetone, the complexes bearing alkyl substituents in one or both *ortho* positions reveal either a moderate amount of *cis* isomer or none at all but their *trans* isomers isomerize when heated in acetonitrile. The results for the heteroleptic system, **15**, show that it is sufficient to have one of the four ligand phenyl *ortho* positions substituted with an alkyl group to enable the *trans–cis* isomerisation.

Obviously, the replacement of one or both *ortho* hydrogen atoms in the phenyl ring by more bulky groups brings about more steric strain in *cis* than in *trans* isomers, thereby stabilising the latter. However, for the *trans* systems the substitution of one or both ligand *ortho* positions by alkyls would, apart from increasing the steric clashes (illustrated by deformations of the azene ring as observed in *trans*-**4** and **5**), remove the intramolecular C–H ··· O bond donors leading to an increase in the free energy of the system. Thus, the *trans* complexes are kinetically destabilised and the isolation of *cis* isomers becomes possible. It is well recognized that an increase in steric strain in the system might lead to a more rapid intramolecular rearrangement.[22]

Finally, it is worth noting that our results for heteroleptic systems show that a given *trans* isomer of a heteroleptic bis-chelate yields the corresponding *cis* isomer as the main product when heated in MeCN, the parent homoleptic *trans*-bis-(chelates) being the minor, but detectable, side products. This implies that the *cis–trans* isomerisation is faster than ligand dissociation, suggesting an intramolecular mechanism.

An additional interesting phenomenon is the ability of solid *cis* systems to undergo a thermal isomerisation, as reported by Chakravorty and co-workers.[4,5]

Stereochemistry of the complexes

A prerequisite for the occurrence of stereoisomerism in square-planar (*SP*-4) complexes, other than the *cis–trans* one, is that they deviate from planarity. This might be achieved by a mutual twist of two essentially planar ligands in the bis-chelate system, leading to a chiral helical structure.[23–25] Another case of stereoisomerism occurs when the strictly planar co-ordination core no longer defines a symmetry plane of the molecule.[26–30] In the latter case the dynamic interconversions of stereoisomers are observed.

The homoleptic triazene-1-oxide bis-chelate may have a symmetry plane in two cases. Either the chelate ring and the ligand aromatic ring are co-planar, or the phenyl ring bearing homomorphic substituents in both *ortho* and *meta* positions, respectively, is perpendicular to a chelate ring. The latter was achieved by use of ligands bearing the phenyl or 2,6-xylyl ring. For the Pd(II) *cis* complexes it is unlikely that the conformation of the ligand is co-planar, for any type of aromatic ring substitution, due to steric reasons. Our NMR results show that a perpendicular orientation of phenyl rings towards the triazene-1-oxide plane is a reasonable representation of the conformation of the ligand in *cis* as well as in *trans* complexes: all homoleptic *cis*- and *trans*-bis(chelates) studied that bear the homomorphically substituted *ortho* positions of aromatic rings reveal that the chelate plane is a symmetry plane of the complex.

If the co-ordinated triazene-1-oxide is devoid of a symmetry plane it displays the axial chirality which might be described using the *aR* and *aS* chirality descriptors.[31] For homoleptic *cis*-bis(chelates) bearing ligands with heteromorphic substituents in *ortho* or *meta* positions of the aromatic rings two conformations are possible: (a) that with both ligands having the same axial chirality, the chiral *cis* complex displaying an effective C_2 symmetry with homomorphic substituents on the aromatic ring located on opposite sides of the molecular plane, or (b) that with the ligands having opposite chirality, the effective symmetry of the *cis* complex being C_s with homomorphic aromatic ring substituents located on the same side of the molecular plane. This situation is illustrated in Fig. 4.

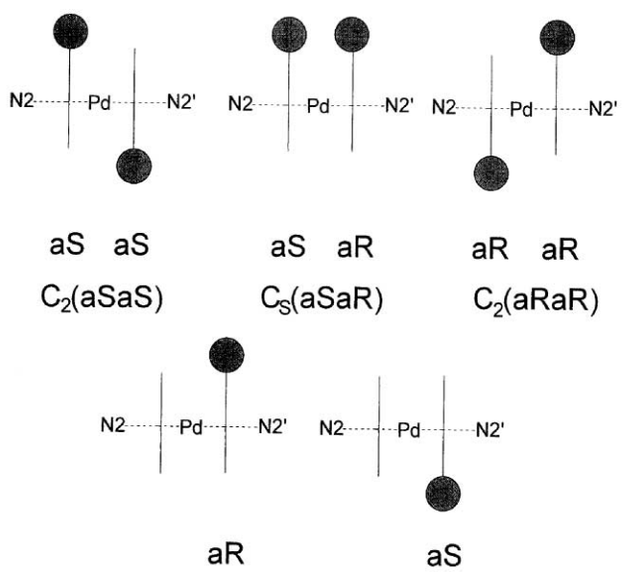

Fig. 4 Schematic represantion of steroisomers in homoleptic (top) and heteroleptic (bottom) triazene-1-oxide *cis*-bis(chelates). The circles represent *ortho* substituents other than hydrogen.

The 180° aromatic ring rotation around the N3–C1 bond of one of the ligands in the C_2 conformation leads to a C_s conformation and subsequent rotation of the second one leads to an enantiomeric C_2 conformation with an opposite sign of ligand axial chirality. It is noteworthy that the same type of stereoisomerism is possible for *trans*-complexes. In this case the symmetry of the achiral stereoisomer is C_i, while it is C_2 for the chiral one.

For heteroleptic bis-chelates three cases are possible: (a) both ligands reveal a symmetry plane and the complex exists in only one conformation revealing the symmetry plane, for example **14**, or (b) one of the ligands reveals a symmetry plane while the other is devoid of it (*cf.* **15**). In this case the system is chiral, its chirality being determined by the axial chirality of the ligand with no symmetry plane. The 180° rotation of the aromatic ring of the latter results in racemization. This situation is depicted in Fig. 4. Finally, (c) both heteromorphic ligands may have no symmetry plane (*cf.* **19**). In this case two chiral diastereoisomers are in principle possible in which both ligands have the same or opposite axial chirality *i.e. aRaR* (*aSaS*) and *aRaS* (*aSaR*). The 180° rotation of the aromatic ring of one of the ligands would result in another diastereoisomer.

Obviously, in the case where two diastereoisomeric conformations are possible it is the steric interactions which are primarily responsible for their relative populations.

Intramolecular dynamics in homoleptic *cis*-bis(chelates)

The ^{1}H NMR spectrum of *cis*-**6** displays one set of resonances at ambient temperature. Lowering the temperature results in a broadening of the resonances in the aromatic region, which give a new pattern with more than four inequivalent protons below 225 K. At 212 K the N*Me* resonance splits into two peaks of virtually the same intensity. This behaviour is indicative of a dynamic equilibrium between two *cis*-species. In the case of *cis*-**8** lowering the temperature resulted in similar behaviour of the aromatic resonances. Additionally, the *N*-isopropylmethyl doublet split into an apparent triplet (doublet of doublets) at 212 K (CD_2Cl_2). In addition, the ^{13}C NMR spectrum at 181 K displayed a doubling of almost all resonances.[32] This behaviour is typical for all homoleptic *cis*-bis(chelates) bearing the asymmetrically substituted *ortho* position in their aromatic rings while no temperature-dependent dynamic behaviour was found for *cis*-**1**. The observed dynamics were therefore proposed to be due to the $C_s \Leftrightarrow C_2$ equilibrium described above.

Within this model one should expect that increasing the steric congestion should result in a differentiation of the free energy of stereoisomers as well as of the rate constant for the reorientation of phenyl rings. Therefore the *cis* isomers of **3** and **9** have been investigated by variable temperature ^{1}H NMR spectroscopy in toluene. Indeed, introducing the second methyl at the same edge of the phenyl ring leads to broadening of the aromatic resonances in the temperature range 294–253 K and splitting of one of the methyl resonances at about 233 K for *cis*-**3**. Additionally, for the latter case a split of the *tert*-butyl resonances at about 1.5 ppm is also found. In the case of *cis*-**9** the same pattern of temperature dependence is observed. The ratio of both stereoisomers for *cis*-**9** was nearly 1 : 1 (as deduced from integration of two separated aromatic methyl substituents), for *cis*-**3** it was 3 : 1 at 233 K (based on deconvolution of *tert*-butyl resonances).

For further corroboration of the proposed model 2D NMR spectra of *cis*-**10** were measured. The ^{1}H NMR spectrum at 294 K in CD_2Cl_2 consists of one set of resonances (see Fig. 5). Decreasing the temperature leads to a broadening of all resonances and then a splitting of the resonances for hydrogens on the substituted phenyl residue. In the first instance the 6-H methyl singlets split into two signals (coalescence point at 258 K), then 2-Me and 5-Me singlets split into two sets (coalescence point 253 K) and finally all phenyl proton peaks become doubled. The ratio of stereoisomers (based on integration of methyl peaks) is 57 : 43 at 205 K.

The full assignment of all peaks has been made on the basis of 2D ^{1}H NMR COSY and NOESY experiments for the CD_2Cl_2 solution at 205 K. The C_s and C_2 stereoisomers bear eclipsed and staggered methyl groups, respectively, on stacked phenyls. The connectivity pattern and observed spatial interactions are shown in Fig. 6. The two NOE contacts between

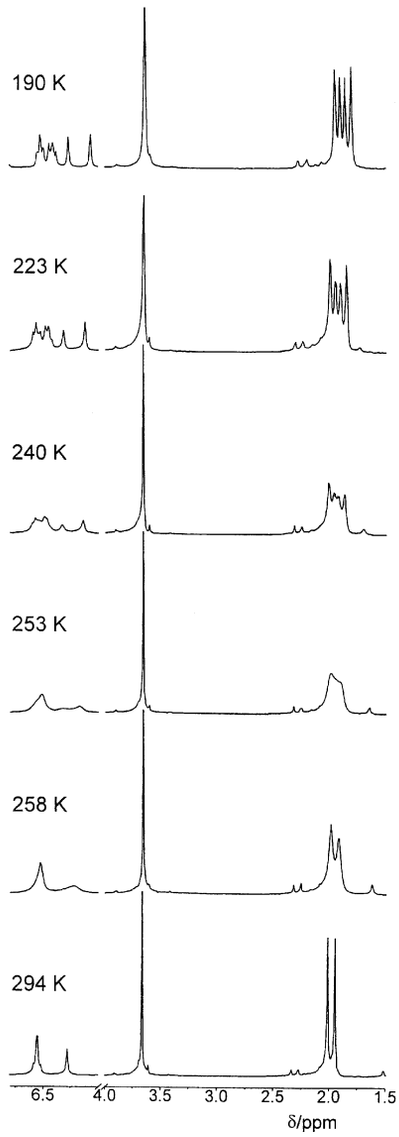

Fig. 5 Temperature dependence of the ^{1}H NMR spectrum of *cis*-$Pd(OMeN_3C_6H_3Me\text{-}2,5)_2$ (**10**) in CD_2Cl_2.

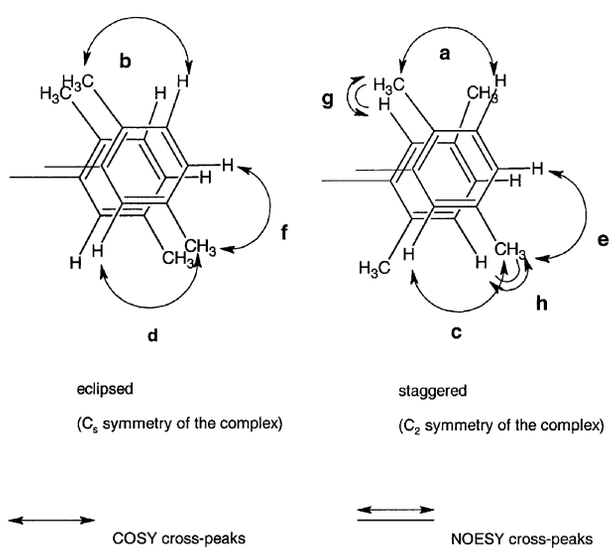

Fig. 6 Connectivity pattern and observed spatial interactions in C_2 and C_s isomers of *cis*-$Pd(OMeN_3C_6H_3Me\text{-}2,5)_2$.

methyl and phenyl ring hydrogens (h and g in Fig. 6) are noteworthy. They correspond to interligand spatial interactions between 2-Me and 6-H (g) and 5-Me and 3-H (h) of the stereo-

isomer displaying the higher population. Thus, this set of resonances was assigned to the C_2 stereoisomer, *i.e.* that revealing a staggered orientation of the phenyl methyl groups. As was mentioned above the concentration of this stereoisomer is higher (57%), the chemical shifts for methyl and phenyl protons are spread over a broader range, all signals being narrower than the resonances of the somewhat less stable C_s isomer. Virtually the same pattern of spectral evolution was found for *cis*-**7**.

In order to observe the effect of enhanced steric congestion the complexes bearing a *tert*-butyl group in their ligand phenyl rings have been studied.

***cis*-3.** The NMR spectrum of this chelate in d_8-toluene reveals the presence of only one species across the entire temperature range. Nevertheless, the *tert*-butyl and aromatic proton resonances display broadening at 294 K, all signals becoming narrower either on decreasing or increasing the temperature, yielding a well resolved set of four signals in the aromatic region together with singlets from NMe and butyl groups. The connectivity pattern and observed spatial interactions are shown in Fig. 7. The COSY spectrum gave the assignment of all signals and the NOESY spectrum revealed the cross-peak between the *tert*-butyl and the 6-H proton, (e in Fig. 7), the latter obviously belonging to the second ligand phenyl (no scalar coupling between Bu^t and 6-H proton is seen).

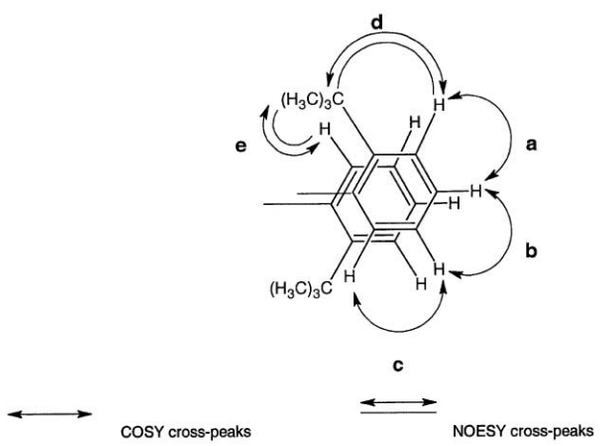

Fig. 7 Connectivity pattern and observed spatial interactions in C_2 and C_s isomers of *cis*-Pd(OMeN$_3$OC$_6$H$_4$Bu^t-2)$_2$.

On the basis of the above observation the C_2 (*aRaR* or *aSaS*) conformation of the complex is inferred with *tert*-butyl groups located on opposite sides of the chelate plane. This conformation is the only one present below 294 K. The broadening of the signals at this temperature might be interpreted in terms of the appearance of a C_s (*aRaS*) conformation bearing both *tert*-butyls on the same side of the chelate plane. The achiral C_s (*aRaR*/*aSaS*) stereoisomer would be a transition state in the process of racemization of the chiral one. Further increase of the temperature seemingly accelerates the racemization process and resonances become narrow.

***cis*-11.** The pattern of temperature dependence on the spectrum of this chelate in d_8-toluene is the same as for its *N*-methyl-substituted analogue **3**. The important feature of the spectrum is the appearance of the diastereotopic splitting of isopropyl methyls observed at 253 K (the difference in chemical shift is merely 0.0051 ppm). This gives a further confirmation of the proposed C_2 chiral conformation of *ortho tert*-butyl substituted chelates. The activation barrier for the racemization process deduced from the temperature of decay of diastereotopic splitting (263 K) was estimated to be 62 kJ mol^{-1}.

Racemization of chiral heteroleptic bis-chelates

As stated previously, the heteroleptic *cis*-bis(chelate) composed of one ligand displaying a symmetry plane and one devoid of it should be chiral. The 180° rotation of the latter should result in racemization of the complex. This pattern was achieved by using ligands bearing the 2,6-xylyl or 4-chlorophenyl aromatic ring as those revealing a symmetry plane and those with 2,4-xylyl and 2-*tert*-butylphenyl rings as those devoid of a symmetry plane. Four systems of this type have been studied. In the *cis*-**15** complex the diastereotopic splitting of isopropyl methyls was observed below 250 K in d_8-toluene solution (see inset in Fig. 8).

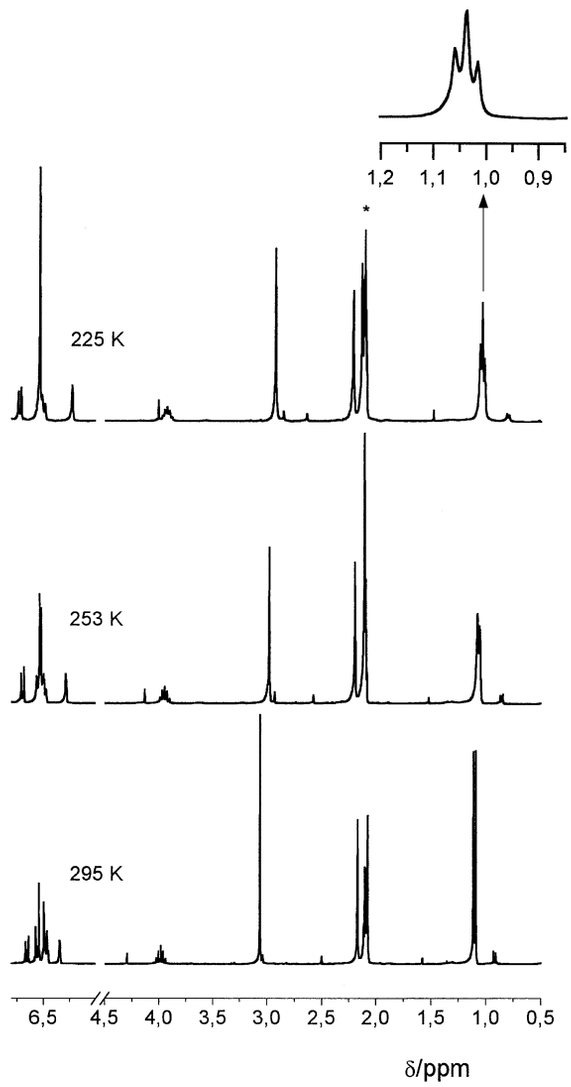

Fig. 8 Diastereotopic splitting of isopropyl methyl signals in *cis*-Pd(OMeN$_3$C$_6$H$_3$Me-2,4)(OPr^{i}N$_3$C$_6$H$_4$Cl-4) (**15**) in d_8-toluene.

This splitting is thus attributed to the presence of two enantiomers with *aR* or *aS* axial chirality for the co-ordinated (OMeN$_3$C$_6$H$_3$Me-2,4)$^-$ ligand. $\Delta G^{\neq}$ of racemization was estimated to be 55 kJ mol^{-1} from the isopropyl resonance coalescence temperature of 250 K. For *cis*-**16** and **17** the pattern of temperature dependence of the NMR spectra in d_8-toluene is essentially the same. Two signals due to the 2- and 4-Me groups of the (OMeN$_3$C$_6$H$_3$Me-2,4)$^-$ ligand and one due to the 2,6-methyls of the N1-isopropyl or ethyl substituted ligand are seen at 294 K. Lowering the temperature results in a slowing of the racemization, yielding differentiation of 2- and 6-methyl signals of both (OEtN$_3$C$_6$H$_3$Me-2,6)$^-$ and (OPr^{i}N$_3$C$_6$H$_4$Cl-4)$^-$ ligands. The activation barriers estimated from coalescence points of the signals are 47 kJ mol^{-1} for **16** and 44 kJ mol^{-1} for **17** (T_c = 230 and 228 K, respectively).

The NMR spectrum of **18** in d_8-toluene solution at elevated temperature (up to 350 K) consists of one set of narrow

resonances. Lowering the temperature produces a broadening of the methyl group resonance as well as some resonances in the aromatic region. These signals split at about 300 K. The isopropyl methyls split into two doublets below 268 K. The dynamics in this system again concern the $aR \Leftrightarrow aS$ racemization process involving the flipping of *tert*-butyl groups between "upward" and "downward" positions relative to the chelate plane. The barrier of racemization (*i.e.* rotation of *tert*-butyl substituted phenyl) is 62 kJ mol^{-1} when deduced from the coalescence point (T_c = 303 K) of the 2,6-methyl signals. 2D experiments at 253 K revealed the interligand NOE cross-peaks between *tert*-butyl protons and one of the *ortho*-methyl protons which identifies the eclipsed methyl group (NOE cross-peak a, Fig. 9) and the strong EXCSY cross-peak (b) between *ortho* methyls.

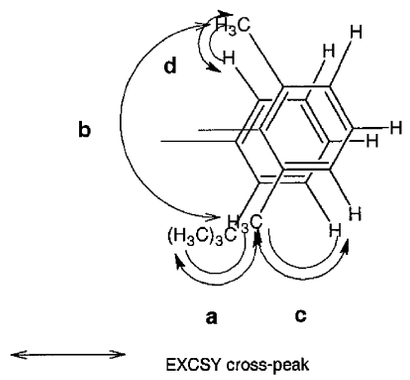

Fig. 9 The observed spatial interactions in *cis*-Pd(OMeN$_3$C$_6$H$_4$Bu^t-2)-(OPr^{i}N$_3$C$_6$H$_3$Me-2,6) (**18**).

Heteroleptic bis-chelates bearing two ligands devoid of a symmetry plane

***cis*-19.** One dominating (*ca.* 90%) set of resonances is observed across the entire temperature range. The 2D spectra allowed the assignment of all resonances in both the aromatic and aliphatic regions. NOE cross-peaks between *tert*-butyl hydrogens and the singlet due to the 6-H′ proton of the (OMeN$_3$C$_6$H$_3$Me-2,5)$^-$ ligand and between *tert*-butyl protons and one of the methyl signals are observed, the latter assigned to the 5-Me group. Therefore the dominant stereoisomer is that with *ortho tert*-butyl and *ortho* methyl groups on the opposite side of the chelate plane, *i.e.* one revealing the same axial chirality for both ligands. Consequently, the second stereoisomer is assigned to that bearing eclipsed *tert*-butyl and 2-Me groups, *i.e.* that with opposite chirality of the ligands. The energy difference between both stereoisomers results from the higher degree of steric congestion in the *aRaS* (*aSaR*) conformer due to the proximity of *ortho tert*-butyl and methyl groups.

***cis*-20.** As stated in the Experimental it was not possible to obtain these chelates in pure form. Nevertheless, the observation of the aliphatic region in the temperature dependent NMR spectra gives an insight into the dynamics of the system. Down to 240 K one set of signals is seen, the diastereotopic splitting of isopropyl methyls occurring below 290 K. The barrier for *tert*-butyl substituted phenyl rotation, *i.e.* the activation energy of racemization, determined from the coalescence point of isopropyl methyls has been estimated to be 65 kJ mol^{-1} (T_c = 286 K). However, below 240 K the *ortho* methyl and *tert*-butyl signals undergo a broadening. At 200 K the second signal of the *tert*-butyl group and one of the *ortho* methyl resonance are separated. The percentage of the new species is *ca.* 10%. This low ratio and broadening of the resonances precluded any reasonable estimation of coalescence point. Consistent with the previous interpretation of the systems in hand the most probable explanation of this observation is the presence of two diastereoisomers of the chelate: the dominating one with neighbouring aromatic rings bearing *ortho* methyl and *tert*-butyl groups on opposite sides of the chelate plane (*i.e.* with the same axial chirality of the ligands) and the less populated one with opposite axial chirality of the ligands revealing the proximity of *tert*-butyl and *ortho* methyl groups. As the diastereotopic splitting of isopropyl signals occurs at a temperature 70 K higher than the separation of the diastereoisomer's signals one infers that the process of racemization involving the rotation of both aromatic rings is slower than the process of diastereoisomeric interconversion involving the rotation of one ring only.

In the *cis* complexes the rotation of the *ortho* substituted aromatic ring is observed even for *tert*-butyl substitution. Molecular modelling shows that the possible pathway of 180° rotation should be that with the co-planar ligand conformation and the bulky group pointing "outside" the whole complex (*i.e.* towards the N2 atom) rather than "inside" (towards the metal and the second ring). Therefore the question arises: is the rotation hindered in *cis* complexes having *both ortho* positions of their ligand phenyls substituted? Hence the complexes of ligands bearing one methyl and one ethyl group in the *ortho* positions of the aromatic rings have been investigated. Again, two *cis* isomers are possible bearing C_2 (*aRaR* or *aSaS*) or C_s (*aRaS*) having the same *ortho* substituents on the opposite or the same side of the chelate plane, respectively. The NMR spectrum of *cis*-**5** reveals the presence of two diastereoisomers of virtually the same concentration. No temperature dependence of the spectral pattern was observed up to 373 K in toluene implying that indeed the substitution of both *ortho* positions of the ligand aromatic ring results in atropoisomerism in *cis* complexes.

Stereodynamics of *trans* complexes

Previously only the stereodynamics of *cis*-bis(chelates) have been discussed. In *trans* complexes of ligands bearing the heteromorphically substituted *ortho* positions of phenyl rings two diastereoisomers can in principle be anticipated; the centrosymmetric one with both homomorphic phenyl substituents placed on opposite sides of the chelate plane and the chiral one, displaying C_2 symmetry with both homomorphic phenyl substituents located on the same side of the chelate plane. The available X-ray data for square-planar triazene-1-oxide bis-chelates show that in solids they adopt uniquely the centrosymmetric or nearly centrosymmetric conformation.[12] It is clear that for complexes studied in this work the possible interconversion between *trans* stereoisomers should be rapid unless significant hindering of rotation about the N3–C1 bond is present. This prompted us to investigate the *trans*-**11** bis-chelate. In fact its NMR spectra in CD_2Cl_2 demonstrate significant broadening of *tert*-butyl and isopropyl methyl resonances. At 181 K the *tert*-butyl signal is split into two of almost equal intensity (53 : 47, by deconvolution of the signals at 1.40 and 1.36 ppm.) The isopropyl methyl resonances are broad, however the pseudo-quartet envelope is clearly seen. It seems reasonable to assume that the observed dynamic behaviour is due to $C_2 \Leftrightarrow C_i$ interconversion. From the temperature of coalescence of *tert*-butyl resonances (T_c = 198 K) the activation energy for the observed process was estimated to be 42 kJ mol^{-1}.

Finally, the *trans*-**5** complex was investigated. The compound isolated from synthesis is a mixture of two possible isomers as indicated by its ^{1}H NMR spectrum which displays the presence of two ethyl methyl groups and a complicated pattern of the ethyl methylenes. Recrystallization of the complex yields solely the centrosymmetric diastereoisomer as demonstrated by X-ray methods (*vide supra*). Dissolving the crystals in chloroform results in the appearance of broadened lines in its NMR spectrum which evolves in a few minutes to a superposition

of two spectra due to two diastereoisomers. Heating of the solution results in broadening of the two ethyl methyl signals which finally coalesce at 319 K. Thus, while the substitution of both *ortho* positions of the ligand aromatic ring in *cis* complexes results in atropoisomerism, for the corresponding *trans* isomers dynamic behaviour is observed.

Conclusions

Systematic studies of a series of homoleptic and heteroleptic palladium triazene-1-oxide bis-chelates have revealed the pronounced effect that the alkyl substituents have on molecular geometry. The interplay of hydrogen bonds, π–π interactions and steric clashes control the ability to undergo geometric isomerisation, the conformation of a given isomer and intermolecular interactions in crystals. The dynamic interconversion between diastereoisomers or enantiomers due to rotation of ligand phenyl rings around the N3–C bond was shown for *cis* and *trans* complexes.

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11 ($OMeC_6H_4Bu^t$-2)H; ^{1}H NMR ($CDCl_3$, 294 K): δ 10.58 (s, 1H, N*H*), 7.56 (d, J = 8.1 Hz, 1H, aromatic), 7.33 (d, J = 7.9 Hz, 1H, aromatic), 7.19 (dd, J = 8.0 Hz, 1H, aromatic), 6.98 (dd, J = 8.0 Hz, 1H, aromatic), 3.97 (s, 3H, N*Me*), 1.45 (s, 9H, CMe_3). ^{13}C NMR ($CDCl_3$, 294 K): δ 138.4, 135.72 (*C*1 + *C*2), 127.84, 127.37, 123.43, 116.75 (*C*3–*C*6), 50.46 (N*Me*), 34.87 (*C*Me_3), 30.84 (C*Me*$_3$).

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13 The angles between the best Pd1–N1–N2–N3–O and C1–C2–C3–C4–C5–C6 planes are 33.8(2), 26.0(2), 40.2(2), and 66.5(1)° for complexes (**1**–**3** and **5**), respectively, and 79.3(2) and 70.8(8)° for **4**.

14 The N2–N3 and N2′–N3′ bond lengths are 1.290(4) and 1.295(4) Å for **4** and 1.304(4) Å for **5** compared to the averaged values of 1.317 (*trans*) and 1.32 Å (*cis*) for the remaining complexes being the shortest of all observed for triazene-1-oxide systems.

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