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The Absolute Configuration of Palladium(II) and Ruthenium(II) Pseudochiral Centers in either Chiral or Achiral Environments

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The *meso*-dithioxamide H-((*R*)-1-(1-phenyl)ethyl)-NSC−CSN-((*S*)-1-(1-phenyl)ethyl)-H (H_2-*meso*DTO) bonds [(η^6-*p*-cymene)chlorido-ruthenium(II)]$^+$ or [(η^3-allyl)-palladium(II)]$^+$ fragment and provides the C_s symmetrical complexes [(η^6-*p*-cymene)ClRu(H-*meso*DTO κ-*S*,*S* Ru)] (**1**) and [(η^3-allyl)palladium(H-*meso*DTO κ-*S*,*S* Pd)] (**2**). These complexes are pseudochiral, and each of them exists as a mixture of two symmetrical meso forms. The improper symmetry of [(η^3-allyl)palladium(H-*meso*DTO κ-*S*,*S* Pd)] has been broken in two different ways: (i) by changing the symmetrical allyl moiety with a η^3-crotyl frame or (ii) by substituting the residual amidic hydrogen in the dithiooxamidate ligand with a M(PR_3)Cl$^+$ fragment (M = Pd or Pt and PR_3 = triorganophosphine). As a consequence, a chiral plane is added to the pseudochiral palladium center, and two pairs of enantiomers are formed in each case. Furthermore, [(η^6-*p*-cymene)chlorido-ruthenium(II)]$^+$ and [(η^3-allyl)-palladium(II)]$^+$ fragments have been joined by means of the binucleating *meso*-dithiooxamidate ligand in a κ-*S*,*S* Ru κ-*N*,*N* Pd coordination mode. The resulting C_s-symmetrical complex [(η^6-*p*-cymene)ClRu(μ-*meso*DTO κ-*S*,*S* Ru κ-*N*,*N* Pd)Pd(η^3-allyl)] (**8**) possesses two pseudochiral metal centers, and it is therefore a mixture of four isomeric meso forms. All of these isomers in a chloroform solution interconvert in that both palladium and ruthenium invert their configurations. A mechanism of epimerization for both palladium and ruthenium is proposed. The absolute configurations of pseudochiral palladium in [(η^3-allyl)(*c*)-Pd(μ-((*R*)-1-(1-phenyl)ethyl)-NSC−CSN-((*S*)-1-(1-phenyl)ethyl) κ-*N*,*N* (*c*)-Pd κ-*S*,*S* (*A*,*C*)-Pd)(*A*,*C*)-Pd(tri^{n}propyl-phosphine)Cl] (**6**) and of pseudochiral palladium and ruthenium in [(η^3-allyl)(*c*)-Pd(μ-((*R*)-1-(1-phenyl)ethyl)-NSC−CSN-((*S*)-1-(1-phenyl)ethyl) κ-*N*,*N* (*c*)-Pd κ-*S*,*S*(s)-Ru)(*s*)-Ru(η^6-isopropyltoluene)Cl] (**8**) are provided. A suitable stereochemical notation is proposed for bimetallic complexes containing pseudochiral centers in either a chiral or an achiral environment.

Introduction

Chirality in metal complexes sometimes arises when a given metal is bonded to suitable ligands as when, for example, a tris-chelate complex is formed from a metal and symmetric chelating ligands; or when a bimetallic complex is prepared from a metalloligand and a metal fragment with a different geometrical environment;[1,2] and also when a square planar complex is obtained by bonding a meso-chelate ligand to a M(AB) fragment (A and B are generic ligands).[3]

As regards the meso ligands, we have already observed that H-((*R*)-phenylethyl)-NSC−CSN-(*S*)-(phenylethyl)-H (hereafter termed H_2-*meso*DTO) bonds a [Ru(*p*-cymene)Cl]$^+$ fragment giving rise to two pseudo-octahedral meso forms depicted in Chart 1.[4]

This means that a meso-chelate ligand creates a stereocenter when bonded to a M(AB) fragment (M = metal ion, A and B = generic ligands, and A ≠ B) in either a square planar or a tetrahedral environment, and therefore these kinds of ligands can be considered prostereogenic.

The ruthenium center in the above formulas has the same stereochemical characteristics as the C_3 carbon in the two trihydroxy glucaric acid (ribaric and xylaric acids, Chart 2), i.e., it is a pseudochiral center.

Pseudochirality is a well-known topic of organic stereochemistry[5] and has been the source of hot debate regarding the apparent paradox of the tetrahedral carbon atom, which

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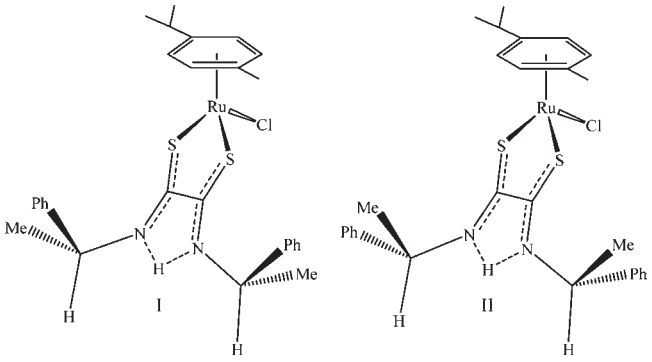
Chart 1. Molecular Structures of the Two Pseudoasymmetric Meso forms of [(η^6-*p*-cymene)ClRu(H-*meso*DTO κ-*S*,*S* Ru)] (**1**)



lies in a symmetry plane despite its four different substituents.[6−13] The intensity of this debate has required repeated interventions by IUPAC in order to provide recommendations for a correct definition of pseudoasymmetry.[11,14,15]

A number of papers have appeared over the past decade on this long-standing issue;[16,17] one in particular dealing with pseudochirality in a very innovative way.[18,19] According to Prelog and Helmchen[8,10] pseudoasymmetry is "... the duality that results from the two ways in which two enantiomorphic ligands can be combined with two enantiotopic half spaces..." Despite this, pseudoasymmetry has attracted little interest in inorganic chemistry, although coordination compounds comprise a great many molecules constituted by two enantiotopic halves, as can be seen in Chart 3.

The present report describes pseudoasymmetry in two different coordination geometries, i.e., in pseudoplanar and pseudooctahedral metal complexes. Thus, the C_s symmetric complexes [(η^6-*p*-cymene)ClRu (H-*meso*DTO κ-*S*,*S* M)] (**1**) and [(η^3-allyl)Pd(H-*meso*DTO κ-*S*,*S* M)] (**2**) have been prepared.

Furthermore, the stereochemistry has been described of [(η^3-crotyl)Pd(H-*meso*DTO κ-*S*,*S* M)] (**3**), which is a chiral complex containing a pseudochiral palladium atom. In addition, the prostereogenic properties of the H_2-*meso*-DTO ligand are highlighted in the chiral complexes *rac*-[(tri^{n}propyl-phosphine)ClPd(H-*meso*DTO κ-*S*,*S* Pd)] (**4**) and *rac*-[(dipheny-2-pyridyl-phosphine)ClPt(H-*meso*DTO κ-*S*,*S* Pt] (**5**). The bimetallic complexes [(tri^{n}propyl-posphine)ClPd(μ-*meso*DTO κ-*S*,*S* Pd-chlorido(phosphine) κ-*N*,*N* Pd-allyl)Pd-(η^3-allyl)] (**6**) and [(diphenyl-2-pyridyl-phosphine)ClPt(μ-*meso*DTO κ-*S*,*S* Pt κ-*N*,*N* Pd)Pd(η^3-allyl)] (**7**) have also been prepared in order to place a pseudochiral palladium in a chiral environment. Lastly, a palladium allyl moiety has been combined with a [Ru(*p*-cymene)Cl]$^+$ fragment in the bimetallic complex [(η^6-*p*-cymene)ClRu (II)(μ-*meso*DTO κ-*S*,*S* Ru κ -*N*,*N* Pd)(η^3- allyl) Pd (II)] (**8**) where both palladium and ruthenium are pseudochiral centers.

Experimental Section

All chemicals were standard reagent grade and were used without further purification. Column chromatography was conducted on aluminum oxide (activated, neutral, Brockman grade I).

^{1}H and ^{13}C NMR spectra were recorded, at room temperature in $CDCl_3$, on a Varian Gemini-300 at 300 and 75 MHz, respectively, and on a VNMRS Varian Instruments at 500 MHz, using the residual proton resonance of the solvent as a δ reference.

The *meso*-dithiooxamide H-((*R*)-1-(1-phenyl)ethyl)-NSC−CSN-((*S*)-1-(1-phenyl)ethyl)-H (H_2-*meso*DTO) was obtained by fractional crystallization from ethanol of an equimolar mixture of *meso*- and *rac*-phenyethyl-dithiooxamide obtained from racemic phenyethyl-amine following a reported procedure.[20]

[(η^6-Cymene)$RuCl_2$]$_2$, [(η^3-allyl)PdCl]$_2$, [(η^3-crotyl)PdCl]$_2$ were commercial products (Aldrich), and *cis*-[$Pt(Me_2SO)_2Cl_2$][21] and [Pd(tri^{n}propyl-phosphine)Cl_2]$_2$[22] were prepared following published methods.

X-ray Crystal Structure Determination of 6 and 8. Suitable X-ray quality orange crystals of both complexes were selected from those crystallized from chloroform/petroleum ether solutions of both **6** and **8**.

Data were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo Kα radiation (λ = 0.71073 Å). Data collection, cell refinement, data reduction and absorption correction were performed by multiscan methods by means of the Bruker software.[23] The structures were solved by direct methods using SIR2004.[24]

The nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2 using SHELXL.[25] All the hydrogen (H) atoms were introduced in calculated positions and constrained to ride on their parent atoms. Selected bond distances and angles are given in Table 1, while the molecular structures are shown in Figures 2 and 3.

General Procedure for the Preparation of Mononuclear Complexes LnM(H-*meso*DTO κ-*S*,*S* M). [LnM = (η^6-*p*-cymene)RuCl (**1**); (η^3-allyl)Pd, (**2**); (η^3-crotyl)Pd (**3**); and (tri^{n}propyl-phosphine)PdCl, (**4**)].

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Chart 2. Two Diastereomeric Meso Forms of Trihydroxy Glucaric Acid: Ribaric (left) and Xylaric (right) Acids

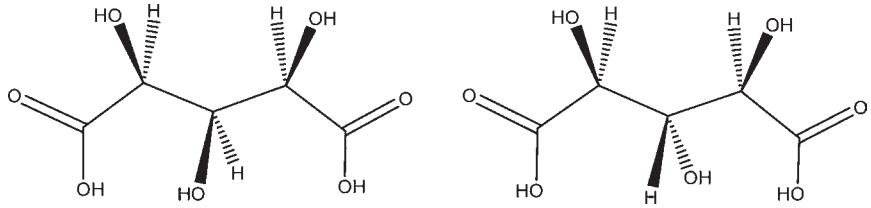
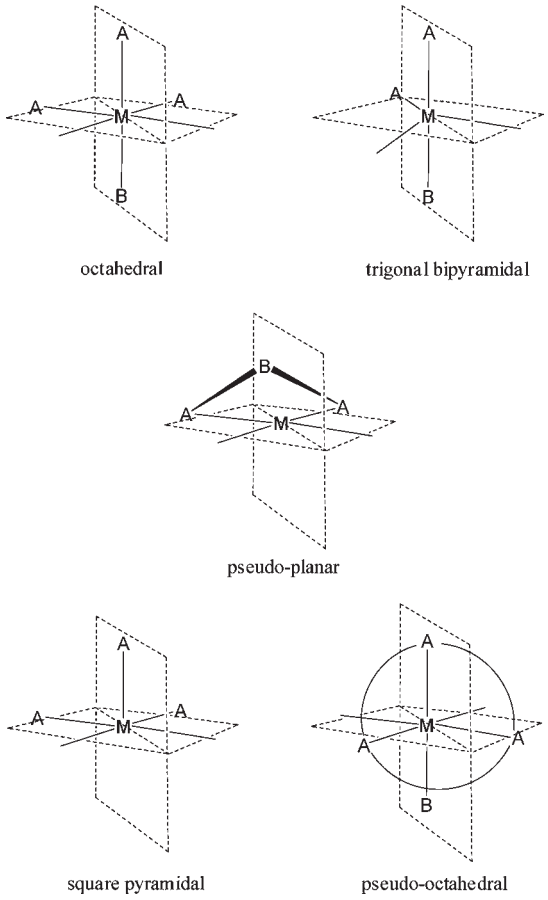


Chart 3. Various Molecular Skeletons Featuring Metal Fragments in a C_s Symmetrical Environment[a]



[a] M is a metal ion, and A and B are generic ligands (A ≠ B). The plane bisecting the angle missing ligand−metal−missing ligand splits each object into two enantiotopic halves in such a way that two enantiomorphic ligands may take the place of the two missing ligands in two different ways, in accordance with the Prelog−Helmchen definition of pseudoasymmetry.

One mmol of $[LnMCl]_2$ was dissolved in chloroform (100 mL), and a half molar amount of H_2-*meso*DTO (0.5 mmol, 164 mg) and sodium bicarbonate (5 mmol, 420 mg) were added. The solutions turned deep red (**1**), bright yellow (**2**, **3**), and orange-red (**4**) and were allowed to stand for 1 h. After this time, the reaction mixture was filtered, the solutions were concentrated to a small volume (ca. 10 mL), and the compounds **1**−**4** were then precipitated by the addition of petroleum ether.

[(η^6-*p*-Cymene)ClRu(H-*meso*DTO κ-*S*,*S* Ru)] (1). Yield: 0.42 g (71%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.30 (m, 10H, N−CH(CH_3)C_6H_5), 5.26 and 5.37 (unresolved AA′XX′ spin system, 4H, cymene−C_6H_4), 5.35 (q, 2H, $^3J_{H-H}$ = 7.0 Hz, N−C*H*(CH_3)C_6H_5), 2.66 (m, 1H, $^3J_{H-H}$ = 7.0 Hz, cymene−C*H*-(CH_3)$_2$), 2.21 (s, 3H, cymene−CH_3), 1.59 (d, 6H, $^3J_{H-H}$ = 7.0 Hz, N−CH(C*H*$_3$)C_6H_5), 1.12 (d, 6H, $^3J_{H-H}$ = 7.0 Hz, cymene−CH(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 179.6 (*C*S), 143.3−128.4 (NCH*C*$_6H_5$), 104.5, 101.5 (cymene−C_q), 85.6, 84.6 (cymene-*C*H), 57.9 (N*C*HC_6H_5), 30.8 (cymene−*C*H(CH_3)$_2$), 22.3 (cymene−CH(*C*H$_3$)$_2$), 21.0 (NCH(*C*H$_3$)C_6H_5), 18.5 (cymene−*C*H$_3$). Anal. calcd for $C_{28}H_{33}N_2S_2ClRu$: H 5.56, C 56.22, N 4.68; Found: H 5.48, C 56.14, N 4.60.

[(η^3-Allyl) Pd (II)(H-*meso*DTO κ-*S*,*S* Pd] (2). Yield: 0.40 g (79%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.32−7.23 (m, 10 H, NCHC_6H_5), 5.37 (q, 2H, $^3J_{H-H}$ = 6.7 Hz, NC*H*C_6H_5), 5.28 and 5.23 (2 m, 1H, allyl−C*H*), 4.11 and 4.09 (2 d, 2H, J_{syn} = 7.1 Hz, *syn*-allyl−CH_2), 2.96 and 2.91 (2d, 2H, J_{anti} = 12.5 Hz, *anti*-allyl−CH_2), 1.58 and 1.57 (2 d, 6H, $^3J_{H-H}$ = 6.7 Hz, NCH-CH_3). ^{13} C NMR (75 MHz, $CDCl_3$), δ (ppm): 181.8 (*C*S), 142.8, 128.6, 127.3, 126.5 (NCH*C*$_6H_5$), 114.0, 113.9, (allyl−*C*H), 62.0, 61.1 (N*C*HC_6H_5), 58.4 (allyl−*C*H_2), 21.8 (NCH(*C*H$_3$)C_6H_5). Anal. calcd for $C_{21}H_{24}N_2S_2Pd$: H 5.09, C 53.10, N 5.90; Found: H 5.19, C 53.01, N 5.99.

[(η^3-Crotyl)Pd (II)(H-*meso*DTO κ-*S*,*S* Pd)] (3). Yield: 0.47 g (65%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.34 (m, 10H, N−CH(CH_3)C_6H_5), 5.44 (m, 2H, N−C*H*(CH_3)C_6H_5), 5.20 (m, 1H, CH_2C*H*CHCH_3), 3.96 (m, 1H, CH_2CHC*H*CH_3), 3.93 and 3.92 (2d, 1H, CH_{syn}H$_{anti}$CHCHCH_3), 2.82 and 2.78 (2d, 1H, CH$_{syn}$*H*$_{anti}$CHCHCH_3), 1.78 and 1.77 (2d, 3H, CH_2CHCH*C*H_3), 1.63, 1.62, 1.62, and 1.61 (4d, 6H, N−CH(C*H*$_3$)C_6H_5).^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 182.5, 182.1, 180.8, 180.4 (*C*S), 143.0, 142.9, 142.8, 142.8 (Ar−C_q), 128.6−126.4 (Ar−*C*H), 114.2, 114.1 (CH_3−CH−*C*H−CH_2), 80.8, 80.7 (CH_3−*C*H−CH−CH_2), 58.3, 58.2, 58.1, 58.0 (N−*C*H(CH_3)C_6H_5), 57.4, 57.5 (CH_3−CH−CH−*C*H_2), 21.9, 21.8, 21.7, 21.5 (N−CH(*C*H$_3$)C_6H_5), 18.5 (*C*H$_3$−CH−CH−CH_2). Anal. Calcd for $C_{22}H_{26}N_2S_2Pd$: H 5.36, C 54.04, N 5.73; Found: H 5.23, C 54.18, N 5.83.

[(Tri″propyl-phosphine)ClPd(H-*meso*DTO κ-*S*,*S* Pd)] (4). Yield: 0.47 g (74%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.25 (m, 10H, N−CH(CH_3)C_6H_5), 5.44 and 5.23 (2q, 2H, N−C*H*(CH_3)C_6H_5), 1.90 (m, 6H, P−CH_2−CH_2−CH_3), 1.69−1.52 (m, 12H, P−CH_2−CH_2−CH_3 and N−CH(C*H*$_3$)C_6H_5), 1.06 (t, 9H, $^3J_{H-H}$ = 7.0 Hz, P−CH_2−CH_2−C*H*$_3$).^{13} C NMR (75 MHz, $CDCl_3$), δ (ppm): 144.5, 139.8, 129.0, 128.3, 128.2, 126.7 (N−CH(CH_3)*C*$_6H_5$), 58.2, 55.0 (N−*C*H(CH_3)C_6H_5), 25.3 (d, $^1J_{P-H}$ = 31.7 Hz, P−*C*H_2−CH_2−CH_3), 22.6, 22.5 (N−CH-(*C*H$_3$)C_6H_5), 17.8 (d, $^3J_{P-H}$ = 2.0 Hz, P−CH_2−CH_2−*C*H_3), 15.8 (d, $^2J_{P-H}$ = 15.2 Hz, P−CH_2−*C*H_2−CH_3). Anal. Calcd for $C_{27}H_{40}N_2PS_2ClPd$: $C_{27}H_{40}N_2PS_2ClPd$: H 6.40, C 51.51, N 4.45; Found: H 6.55, C 51.73, N 4.38.

Synthesis of [(Dipheny-2-pyridyl-phosphine)ClPt(H-*meso*-DTO κ-*S*,*S* Pt] (5). One mmol (422 mg) of *cis*-Pt $(Me_2SO)_2Cl_2$ was suspended in chloroform (100 mL) and then reacted with an equimolar amount of (diphenyl-2-pyridyl-phosphine) (1 mmol, 263 mg). A yellow solution was obtained containing an equilibrium mixture of *cis*-$PtCl_2(Me_2SO)$(diphenyl-2-pyridyl-phosphine) and Pt(diphenyl-2-pyridyl-phosphine κ-P,N Pt)Cl_2.[26] The yellow solution was reacted with 338 mg (1 mmol) of H_2-*meso*DTO. The solution turned deep red due to the formation of the ion pair {[(Pt(H_2-*meso*DTO κ-*S*,*S* Pt)(diphenyl-2-pyridyl-phosphine)-Cl]$^+$,(Cl^-)}. The deep red solution was reacted with 5 mmol (420 mg) of sodium bicarbonate in order to dehydrohalogenate

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Table 1. Significant Bond Lengths (Å) and Angles (°) for **6** and **8**

6		**8**	
Pd(1)−N(1)	2.091(2)	Pd(1)−N(1)	2.089(4)
Pd(1)−N(2)	2.094(2)	Pd(1)−N(2)	2.094(4)
Pd(1)−C(3)	2.117(3)	Pd(1)−C(3)	2.105(6)
Pd(1)−C(4)	2.106(3)	Pd(1)−C(4)	2.125(6)
Pd(1)−C(5)	2.122(2)	Pd(1)−C(5)	2.125(5)
C(3)−C(4)	1.337(5)	C(3)−C(4)	1.344(10)
N(2)−C(2)	1.295(3)	N(2)−C(2)	1.273(6)
C(1)−S(1)	1.722(2)	C(1)−S(1)	1.716(5)
N(2)−C(14)	1.477(3)	N(2)−C(14)	1.486(6)
N(1)−C(1)	1.296(3)	N(1)−C(1)	1.269(6)
C(4)−C(5)	1.361(4)	C(4)−C(5)	1.396(9)
C(2)−S(2)	1.721(2)	C(2)−S(2)	1.733(5)
N(1)−C(6)	1.483(3)	N(1)−C(6)	1.478(6)
C(1)−C(2)	1.503(3)	C(1)−C(2)	1.524(7)
Pd(2)−S(1)	2.2477(6	S(1)−Ru	2.3607(18)
Pd(2)−S(2)	2.3260(6)	S(2)−Ru	2.3641(15)
Pd(2)−Cl	2.3376(6)	Ru−Cl	2.4247(15)
Pd(2)−P	2.2741(6)	Ru−CT	1.6935(4)
N(1)−Pd(1)−N(2)	77.45(7)	N(1)−Pd−N(2)	77.39(16)
N(1)−Pd(1)−C(3)	107.0(1)	N(1)−Pd−C(3)	106.0(2)
N(2)−Pd(1)−C(5)	107.00(9)	N(1)−Pd−C(5)	173.8(2)
C(3)−Pd(1)−C(5)	68.7(1)	C(3)−Pd−C(5)	68.6(3)
C(1)−N(1)−C(6)	119.3(2)	C(1)−N(1)−C(6)	119.8(4)
C(1)−N(1)−Pd(1)	114.2(1)	C(1)−N(1)−Pd	115.9(3)
C(6)−N(1)−Pd(1)	125.6(1)	C(6)−N(1)−Pd	124.3(3)
C(2)−N(2)−C(14)	119.8(2)	C(2)−N(2)−C(14)	119.6(5)
C(2)−N(2)−Pd(1)	114.9(1)	C(2)−N(2)−Pd	115.3(3)
C(14)−N(2)−Pd(1)	125.1(1)	C(14)−N(2)−Pd	125.1(3)
N(1)−C(1)−C(2)	116.1(2)	N(1)−C(1)−C(2)	115.2(4)
N(1)−C(1)−S(1)	124.1(2)	N(1)−C(1)−S(1)	127.1(4)
C(2)−C(1)−S(1)	119.8(2)	C(2)−C(1)−S(1)	117.7(4)
N(2)−C(2)−C(1)	114.9(2)	N(2)−C(2)−C(1)	115.6(4
N(2)−C(2)−S(2)	125.6(2)	N(2)−C(2)−S(2)	126.1(4)
C(1)−C(2)−S(2)	119.4(2)	C(1)−C(2)−S(2)	118.3(4)
C(3)−C(4)−C(5)	124.8(4)	C(3)−C(4)−C(5)	120.9(7)
S(1)−Pd(2)−P	92.07(2)	C(1)−S(1)−Ru	104.12(19)
S(1)−Pd(2)−S(2)	88.96(2)	C(2)−S(2)−Ru	103.11(17)
P−Pd(2)−Cl	88.30(2)	CT−Ru−S(1)	130.70(4)
S(2)−Pd(2)−Cl	90.75(2)	CT−Ru−S(2)	129.93(4)
		S(1)−Ru−S(2)	83.42(6)
		CT−Ru−Cl	124.20(6)
		S(1)−Ru−Cl	87.35(7)
		S(2)−Ru−Cl	86.26(6)
Pd(1)−N(1)−C(6)−C(7)	−73.2(2)	Pd−N(1)−C(6)−C(7)	−76.2(5)
Pd(1)−N(2)−C(14)−C(15)	84.6(2)	Pd(1)−N(2)−C(14)−C(15)	−43.0(7)
Pd(1)−N(1)−C(6)−C(8)	54.4(2)	Pd−N(1)−C(6)−C(8)	52.8(7)
Pd(1)−N(2)−C(14)−C(16)	−41.3(2)	Pd(1)−N(2)−C(14)−C(16)	−43.0(7)
N(1)−C(6)−C(8)−C(13)	51.2(3)	N(1)−C(6)−C(8)−C(13)	36.3(8)
N(2)−C(14)−C(16)−C(17)	−39.3(3)	N(2)−C(14)−C(16)−C(17)	−52.9(7)
N(1)−C(1)−C(2)−N(2)	1.4(3)	N(1)−C(1)−C(2)−N(2)	−1.6(7)

the ion pair, and the solution rapidly turned orange. After concentration (ca. 10 mL), petroleum ether was added, and [(diphenyl-2-pyridyl-phosphine)ClPt(H-*meso*DTO *κ-S,S* Pt] was collected as an orange powder. Yield: 0.62 g (75%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.70 (m, 1H, pyr−H_6); 8.38 (m, 1H, pyr−H_3), 7.80−7.00 (m, 22H, Ar−*H* and pyr−*H*), 5.35 and 4.72 (2q, 2H, $^3J_{H-H}$ = 6.6 Hz, NC*H*(CH_3)C_6H_5), 1.64 and 1.38 (2d, 3H, $^3J_{H-H}$ = 6.6 Hz, NCH(CH_3)C_6H_5). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 182.4, 180.7 (*C*S), 148.6−126.3 (29C, Ar*C* and pyr*C*), 58.2, 57.5 (N*C*H$CH_3C_6H_5$), 21.9, 18.6 (NCH*C*$H_3C_6H_5$). Anal. calcd for $C_{35}H_{33}N_3PS_2ClPt$: H 4.05, C 51.18, N 5.12; Found: H 4.12, C 51.24, N 5.24.

Synthesis of [(Tri^{n}propyl-phosphine)ClPd(*μ-meso*DTO *κ-S,S* Pd-chlorido(phosphine) *κ-N,N* Pd-allyl)Pd(η^3-allyl)] (6). Procedure A: 1 mmol (630 mg) of [(tri^{n}propyl-phosphine)ClPd (II)-(H-*meso*DTO *κ-S,S* Pd)] was dissolved in chloroform (100 mL), and a half-molar quantity of [(η^3-allyl)PdCl]$_2$ (0.5 mmol, 183 mg) was then added. The mixture was refluxed at 50 °C for 1 h. The solvent was removed, and the crude product was dissolved in the minimum amount of chloroform and loaded on an alumina column equilibrated with petroleum ether. The pure [(tri^{n}propyl-phosphine)ClPd(*μ-meso*DTO *κ-S,S* Pd-chlorido(phosphine) *κ-N,N* Pd-allyl)Pd(η^3-allyl)] was separated in the yellow portion of the eluate ($CHCl_3$/petroleum ether 50% v/v).

Procedure B: 1 mmol (475 mg) of [(η^3-allyl) Pd (II)(H-*meso*-DTO *κ-S,S* Pd] was dissolved in chloroform (100 mL), and a half-molar quantity of [(tri^{n}propyl-phosphine)PdCl$_2$]$_2$ (0.5 mmol, 337 mg) was then added. The mixture was refluxed at 50 °C for 1 h. The solvent was removed, and the crude product was dissolved in the minimum amount of chloroform and loaded on an alumina column equilibrated with petroleum ether. The pure [(tri^{n}propyl-phosphine)ClPd(*μ-meso*DTO *κ-S,S* Pd-chlorido-(phosphine) *κ-N,N* Pd-allyl)Pd(η^3-allyl)] was separated in the yellow portion of the eluate ($CHCl_3$/petroleum ether 50% v/v).

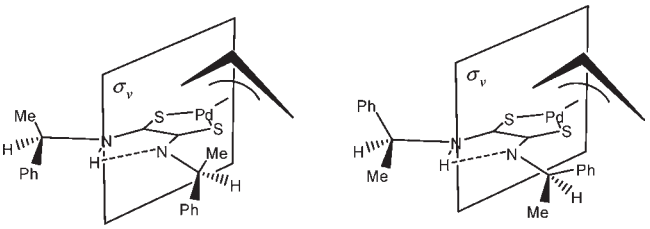
Yield: 1.04 g (67%) (procedure A); 0.56 g (73%) (procedure B). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.20 (m, 10H, N−CH(CH_3)C_6H_5), 5.89 and 5.81 (2 m, 2H, N−C*H*(CH_3)C_6H_5), 4.78 and 4.20 (2 m, 1H, allyl−C*H*), 3.19, 3.16, 2.53, and 2.50 (4 d, 2H, $^3J_{syn}$ = 7.4 Hz, *syn*-allyl−CH_2), 2.35 and 2.30 (2 d, 1H, $^3J_{anti}$ = 13.1 Hz, *anti*-allyl−CH_2), 1.84 (m, 6H, P−CH_2−CH_2−CH_3), 1.66

(m, 6H, P−CH_2−CH_2−CH_3), 1.60, 1.56, 1.50, and 1.46 (4d, 6H, $^3J_{H-H}$ = 6.5 Hz, N−CH(CH_3)C_6H_5), 1.27 and 1.26 (2d, 1H, $^3J_{anti}$ = 13.1 Hz, *anti*-allyl−CH_2), 1.05 and 1.04 (2 t, 9H, $^3J_{H-H}$ = 7.0 Hz, P−CH_2−CH_2−CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 192.3, 191.9, 190.1, 189.7 (*C*S), 146.0, 143.6, 128.1, 127.9, 126.8, 126.7, 126.6, 126.5, (N−CH(CH_3)C_6H_5), 112.3, 111.3 (allyl−*C*H), 58.9, 58.4 (N−*C*H(CH_3)C_6H_5), 58.3, 58.1, 57.9, 57.7 (allyl−CH_2), 24.8 (d, $^1J_{P-H}$ = 27.5 Hz, P−CH_2−CH_2−CH_3), 17.8 (d, $^3J_{P-H}$ = 2.0 Hz, P−CH_2−CH_2−*C*H$_3$), 17.2, 17.0 (N−CH(*C*H$_3$)-C_6H_5), 15.8 (d, $^2J_{P-H}$ = 14.5 Hz, P−CH_2−*C*H$_2$−CH_3).). Anal. calcd for $C_{30}H_{44}N_2PS_2ClPd_2$: H 5.71, C 46.43, N 3.61; Found: H 5.59, C 46.07, N 3.78.

Synthesis of [(Diphenyl-2-pyridyl-phosphine)ClPt(*μ*-*meso*-DTO *κ*-*S*,*S* Pt *κ*-*N*,*N* Pd)Pd(*η*^{3}- allyl)] (7). One mmol (366 mg) of [Pd(η^3-allyl)(μ-Cl)$_2$] was dissolved in a chloroform/methanol mixture (30 mL, 70:30 v/v) and reacted with a half-molar quantity (2 mmol, 1.44 gr) of [2-(dipheny-2-pyridyl-phosphine)ClPt(H-*meso*DTO *κ*-*S*,*S* Pt]. The solution, which turned deep red, was allowed to stand for 2 h. The solvents were removed, and the crude product was dissolved in chloroform (10 mL) and loaded on an alumina column equilibrated with petroleum ether. The desired product was collected as orange eluate ($CHCl_3$/petroleum ether 50% v/v) and concentrated to a small volume (1 mL). The bimetallic complex precipitated as orange powder upon addition of petroleum ether 40−60 (30 mL). Yield: 1.38 g (80%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.72 (m, 1 H, pyr−H_6), 8.52 (m, 1 H, pyr−H_3), 7.87−7.05 (m, 22 H, Ar−*H* and pyr−*H*), 5.83, 5.83, 5.15, and 5.13 (4q, 2H, $^2J_{H-H}$ = 6.6 Hz, NC*H*C_6H_5), 4.73 and 4.21 (2 m, 1H, allyl−C*H*), 3.17, 3.09, 2.52, and 2.47 (4d, 2H, J_{syn} = 7.0 Hz, *syn*-allyl−CH_2), 2.33 and 2.31 (2d, 1H, J_{anti} = 12.7 Hz, *anti*-allyl−CH_2), 1.56, 1.45, 1.36, and 1.24 (4d, 6H, $^2J_{H-H}$ = 6.6 Hz, CH_3), 1.22 and 1.18 (2d, 1H, J_{anti}= 12.7 Hz, *anti*-allyl−CH_2). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 190.8, 190.4, 190.1, 189.8 (*C*S), 154.6−124.4 (29C, Ar−*C* and pyr−*C*), 112.3, 111.4 (allyl−*C*H), 60.5, 60.4, 59.9, 59.8 (N*C*HPh), 58.2, 58.1, 58.0, 57.9 (allyl−CH_2), 17.9, 17.8, 16.9, 16.7 (CH_3). Anal. calcd for $C_{38}H_{37}N_3PS_2ClPdPt$: H 3.85, C 47.16, N 4.34; Found: H 3.95, C 47.33, N 4.41.

Synthesis of [(*η*^{6}-*p*-Cymene)ClRu (II)(*μ*-*meso*DTO *κ*-*S*,*S* Ru *κ* -*N*,*N* Pd)(*η*^{3}-allyl) Pd (II)] (8). One mmol (366 mg) of [Pd(η^3-C_3H_5)(μ-Cl)$_2$] was dissolved in a chloroform/methanol mixture (30 mL, 70:30 v/v) and reacted with a two-fold amount (2 mmol, 1.20 g) of the [(η^6-*p*-cymene)ClRu(H-*meso*DTO *κ*-*S*,*S* Ru)] complexes. The solution, which turned deep red, was allowed to stand for 2 h. The solvents were removed, and the crude product was dissolved in the minimum amount of chloroform (10 mL) and loaded on an alumina column equilibrated with petroleum ether. The desired product was collected as an orange eluate and concentrated to a small volume (1 mL). The bimetallic complex precipitated as orange powder upon adding petroleum ether 40−60 (30 mL). Yield: 1.07 g (72%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.37−7.07 (m, 10 H, N−CH(CH_3)C_6H_5), 5.93 (m, 2H, N−C*H*(CH_3)C_6H_5), 5.34 (m, 4H, cymene−C_6H_4), 4.69, 4.63, 4.24, and 4.02 (4m, 1H, allyl−C*H*), 3.07, 3.02, 2.51, and 2.30 (4d, 2H, J_{syn} = 6.9 Hz, *syn*-allyl−CH_2), 2.83 (m, 1H, cymene−C*H*(CH_3)$_2$), 2.27 and 2.13 (2d, 2H, J_{anti} = 12.6 Hz, *anti*-allyl−CH_2, the remaining two doublets at higher field are buried under CH_3 signals), 2.24, 2.23, 2.22, and 2.20 (4s, 3H, cymene−CH_3); 1.55, 1.54, 1.45, and 1.44 (4d, 6H, $^2J_{H-H}$ = 6.5 Hz, N−CH-(CH_3)C_6H_5), 1.27, 1.26, 1.25, and 1.22 (4d, 6H, $^2J_{H-H}$ = 6.9 Hz, cymene−CH(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 191.3, 191.3, 191.25, 190.9 (*C*S), 143.8, 143.8, 143.6, 143.51 (C_q), 128.0−126.0 (12C, *C*H), 111.2, 110.8, (allyl−*C*H), 103.6, 103.6, 101.3, 101.2, (cymene−C_q), 85.5, 85.5, 85.5, 85.4, 84.1, 84.0, 84.0, 83.8 (*C*H), 61.1, 61.0, 60.8, 60.7 (N*C*HCH$_3$), 57.4, 57.3, 57.1, 57.0, (allyl−CH_2), 31.0, 30.9 (cymene−*C*H(CH_3)$_2$), 22.6, 22.5, 18.6, (cymene−CH(*C*H$_3$)$_2$), 19.2, 18.2, 18.0, 17.2 (NCH*C*H$_3$). Anal. calcd for $C_{31}H_{37}N_2S_2ClRuPd$: H 5.01, C 50.00, N 3.76; Found: H 5.09, C 50.28, N 3.62.

Chart 4. Molecular Structures of the Two Pseudoasymmetric Meso Forms of [(η^3-Allyl)Pd(H-*meso*DTO *κ*-*S*,*S* Pd)] (**2**)[a]



a *c*

[a] The symmetry planes σ_v are highlighted, and *a* and *c* are the stereochemical descriptors.

Results and Discussion

Mononuclear complexes. [L_nM(H-*meso*DTO *κ*-*S*,*S* M)] (L_nM = (η^6-*p*-cymene)RuCl (**1**) and (η^3-allyl)Pd (**2**)) were obtained by the following process:

$$2H_2 meso\text{DTO} + [L_nMCl]_2 \rightarrow 2[L_nM(\text{H-}meso\text{DTO}\kappa\text{-}S, S\text{M})] + 2HCl$$

Compound (**1**) (L_nM = (η^6-*p*-cymene)RuCl) was previously reported as an equimolar meso/rac mixture from a dithioxamide prepared from racemic phenylethylamine,[4] although the symmetrical diastereomers were not separated from the chiral ones.

The synthesis of (**1**) has been now performed from isomerically pure *meso*-dithioxamide, and the meso forms indicated in Chart 1 have been obtained. Their NMR spectra show isochronous resonances for both pseudochiral diastereomers. The *r*/*s* descriptors of pseudoasymmetric carbon atoms can be used to indicate the two diastereoisomers in Chart 1. Such descriptors are invariant upon reflection in a mirror but are reversed if any of the ligand entities are exchanged (i.e., *r* becomes *s* and vice versa). Thus, the species I and II in the Chart 1 are the *r* and the *s* isomer, respectively.

The stereochemistry of ruthenium in [(η^6-*p*-cymene)-ClRu(H-*meso*/*rac*DTO *κ*-*S*,*S* M)] is analogous to that of the C_3 carbon in the two meso forms of trihydroxy glucaric acid (Chart 2), so that ruthenium in the abovementioned compound is also a stereogenic achirotopic center .[27]

Compound (**2**) (L_nM = (η^3-allyl)Pd) exhibits C_s symmetry, and it is therefore made up of two enantiotopic halves, with respect to which the enantiomorphic substituents of the meso ligand can be arranged in two different ways, according to the Prelog−Helmchen definition[8,10,13] (Chart 4).

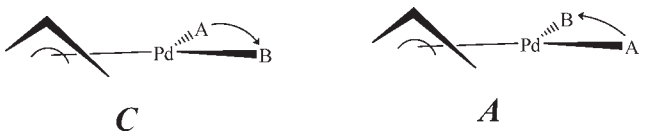
In contrast, allyl-palladium complexes containing two different generic ligands, A and B (A ≠ B), are chiral and give rise to a pair of enantiomers as shown in Chart 5.

In such complexes, the palladium atom is a stereocenter since its configuration is reversed in the exchange of the A, B ligands as well as by the pseudorotation of the allyl group.

The configuration of the above enantiomers can be indicated with the *A*/*C* descriptors,[2,28] although other effective nomenclatures have subsequently been exploited

(27) Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3319–3328.

Chart 5. Schematic View of a (η^3-Allyl) Palladium Enantiomeric Pair with a Symmetrical Allyl Group[a]



[a] A and B are generic ligands (A ≠ B). *A* and *C* are the chiral descriptors. When the molecule is viewed from the central allyl carbon towards palladium, the other two atoms coordinated to the metal, A and B (with decreasing CIP priority), follow a clockwise direction in (*C*), whereas these atoms follow an anticlockwise direction in (*A*).

to describe the stereochemistry of this type of compound.[29] Thus, in the pseudoplanar complexes [(η^3-allyl)Pd-(H-*meso*DTO) κ-*S*,*S* Pd)] (**2**) palladium has the same stereochemical characteristics of a pseudoasymmetric carbon atom, i.e., it belongs to a symmetric molecule despite the two different substituents being placed opposite to the allyl group. In other words, the central palladium in [(η^3-allyl)Pd(H-*meso*DTO) κ-*S*,*S* Pd)] is pseudochiral. Hence, the palladium meso forms shown in Chart 4 can be indicated by *a*/*c* descriptors, which are derived from the *A*/*C* ones used to term chiral molecules, like those in Chart 5.

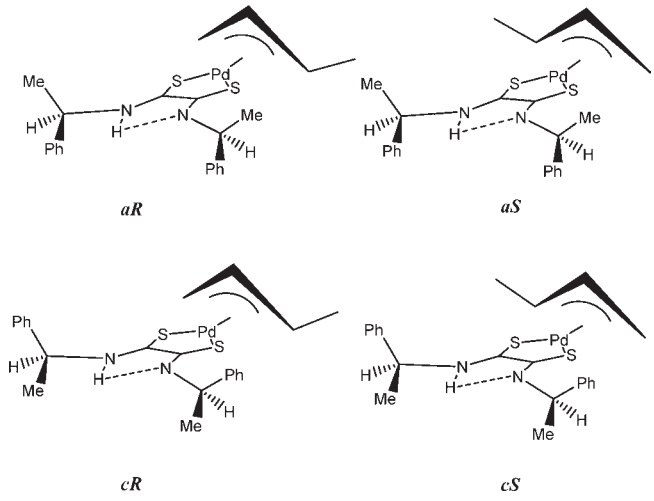
We suggest the use of *a*/*c* descriptors in compliance with the *r*/*s* descriptors exploited for pseudoasymmetric carbon atoms; in both cases, the pseudochiral descriptors are the corresponding chiral ones written in lower case. Like *r*/*s*, *a*/*c* descriptors are also invariant on reflection in a mirror but are reversed in the exchange of the two enantiomorphic groups as well as in the exchange of two ligands in any one of the CH_2 carbon atoms of the allyl group.

NMR spectra of [(η^3-allyl)Pd(H-*meso*DTO κ-*S*,*S* Pd)] (**2**) show most of the signals split due to the presence of two diastereomers in solution. The improper symmetry of [(η^3-allyl)Pd(H-*meso*DTO κ-*S*,*S* Pd)] (**2**) can be broken by replacing one of the terminal hydrogen atoms in the allyl group. This can easily be accomplished by reacting [(η^3-crotyl)PdCl]$_2$ with a two-fold amount of H_2-*meso*DTO.

In the resulting [(η^3-crotyl)Pd(H-*meso*DTO κ-*S*,*S* Pd)] (**3**), palladium is still a pseudochiral center, since in the two possible diastereomers, the R benzyl group may be placed at either the left- or the right-hand side with respect to the crotyl CH cuspid. Furthermore, each diastereomer can be envisaged as a racemate, in that crotyl CH_3 can be placed at either the left- or the right-hand side with respect to the crotyl CH cuspid (Chart 6).

Indeed, both ^{1}H and ^{13}C NMR spectra show resonances corresponding to the presence of a pair of diastereomers in solution. On this basis, we have envisaged two

Chart 6. Molecular Structures of the Four Stereomers of the Complex [(η^3-Crotyl)Pd(H-*meso*DTO κ-*S*,*S* Ru)] (**3**)[a]



[a] The stereochemical descriptors of the pseudochiral palladium center and of the crotyl chiral plane are *a*,*c* and *R*,*S*(see text).

stereogenic elements in (**3**). One of them is the pseudochiral palladium atom,[30] the other is the chiral plane determined by the coplanar crotyl sp^2 carbon atoms. These sp^2 carbons establish a unique stereogenic element in that the interchange of ligands in any one of them leads to the same enantiomer . In other words, a palladium−crotyl compound looks like a sort of unsymmetrically substituted piano stool complex so that it can exist as a pair of enantiomers even when the other substituents are two identical generic ligands A (Chart 7).

Summing up, the chirality of square planar palladium allyl complexes have hitherto been described by means of a chiral center,[29] axis,[31] or plane[2] (i.e., the molecular square plane); however, none of these previously reported approaches are suitable for describing the chirality of complexes of the type [(η^3-crotyl)PdA$_2$] (A = a generic ligand).

Thus, the stereochemical descriptors for crotyl chiral planes that we have chosen are the ones previously adopted for metallocenes and other π-arene metal compounds by applying an extension of the so-called CIP rule[32,33] to substituted and metal-bound sp^2 carbons (Chart 7).

On the basis of the above, the four isomers in the Chart 6 can properly be named with the following combinations: *aR*, *aS*, *cR*, and *cS*. Diastereomers resulting from the simultaneous presence of both chiral molecular and allyl planes in a palladium allyl complex are generally indicated by means of a combination of endo−exo and syn−anti descriptors.[34−41] This method is currently being used and is quite user-friendly. However, it seems unsuitable to describe the stereochemistry of complexes, like the ones reported in this paper, since they do not show clear reference points out of the Pd(H-*meso*DTO) plane.

(28) The chirality symbols *C* (clockwise) and *A* (anticlockwise) are used to denote absolute stereochemistry in coordination compounds, except that *R* and *S* are used for tetrahedral complexes (T-4) and Δ and Λ for octahedral complexes with three bidentate or two bidentate ligands in a skew configuration. (See also: IUPAC Rule 7.8, *Pure Appl. Chem.* **1971**, *28*, 75).

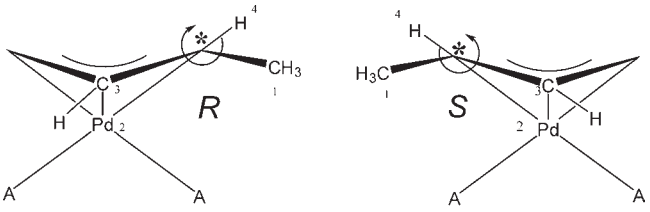
(29) (a) Faller, J. W.; Sarantopoulos, N. *Organometallics*. **2004**, *23*, 2008–2014. (b) Faller, J. W.; Stokes-Huby, H. L.; Albrizzio, M. A. *Helv. Chim. Acta* **2001**, *84*, 3031–3042.

(30) In 2 and 3 the two benzylic carbon atoms are also stereocenters, but they configure palladium as a stereocenter only when they have opposite configuration. Stereomers having benzylic carbon in the same configuration do not contain palladium as a pseudoasymmetric center, and therefore, they have not been taken into consideration in this paper.

(31) (a) Hayashi, T.; Kawatsura, M.; Uozumi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1681–1687. (b) Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y.; Miki, M.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 775–776. (c) Hayashi, T.; Iwamura, H.; Uozumi, Y.; Matsumoto, Y.; Ozawa, F. *Synthesis* **1994**, 526.

(32) Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1–36.

Chart 7. Schematic View of a (η^3-Allyl) Palladium Enantiomeric Pair with an Asymmetrical Allyl Group[a]

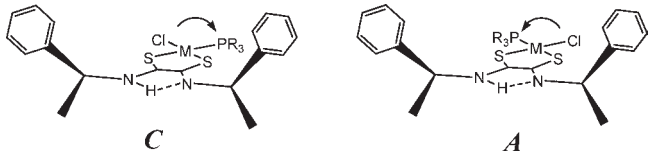


[a] A is a generic ligand. *R* and *S* are the stereochemical descriptors for chiral planes determined by the metal-bonded sp^2 carbons. The carbon atom bearing the substituent with the higher atomic number is considered virtually tetrahedral (ref 5a, p. 1122).

A chelate ligand, like H_2-*meso*DTO, bonds a $M(PR_3)Cl$ frame (M = Pt(II) and Pd(II), and PR_3 = triorganophosphine) in a square planar arrangement. As a consequence, the improper symmetry of the ligand is broken, and the resulting complexes [(H-*meso*DTO κ-*S*,*S* M)M-$(PR_3)Cl$] are chiral. In fact, the reaction of H_2-*meso*DTO with an equimolar amount of *cis*-$[Pt(Me_2SO)(PN)Cl_2]$ or a half-molar quantity of $[PtP(tri^npropyl)_3Cl_2]_2$ in the presence of sodium bicarbonate affords [(H-*meso*DTO κ-*S*,*S* M)$M(PR_3)Cl$] complexes as racemic mixtures in a high yield.

The configuration of [(H-*meso*DTO) κ-*S*,*S* M)M-$(PR_3)Cl$] complexes can be described by viewing the molecule from the enantiomorphic groups of the meso ligand oriented in such a way that the substituents of higher priority (phenyl groups) are oriented upward with respect to the molecular plane. Then, we suggest indicating the enantiomers of the racemate by means of the direction *C* (clockwise) or *A* (anticlockwise) of the decreasing CIP priority sequence of the monodentate ligands on M (Chart 8). This method is reminiscent of the assessment of the stereochemistry in chiral planar complexes suggested by Wild.[3]

Chart 8. Schematic View of the Enantiomers [(PR_3)ClM(H-*meso*DTO κ-*S*,*S* M] (M = Pd, PR_3 = tri-^{n}propyl-phosphine, M = Pt, and PR_3 = diphenyl-2-pyridyl-phosphine)[a]



[a] *C* and *A* are planar chirality descriptors.

Bimetallic complexes. The racemate [(H-*meso* DTO κ-*S*,*S* M)$M(PR_3)Cl$] ($M(PR_3)Cl$ = (tri^{n}propyl-phosphine)-ClPd (**4**): $M(PR_3)Cl$ = dipheny-2-pyridyl-phosphine)-ClPt (**5**)] are metalloligands which are able to substitute the residual amidic hydrogen N−H···N of the *S*,*S* chelated dithiooxamidate with a metal frame $[M'L_n]^+$ (M′ = bi or trivalent metal ion, and L_n = set of neutral and/or anionic ligands) in line with well-established synthetic procedures.[1,2,42−44] Thus, by reacting [(H-*meso*DTO κ-*S*,*S* M)$M(PR_3)Cl$] with a half-molar quantity of $[(\eta^3$-allyl)$PdCl]_2$, the heterobimetallic complexes [[(η^3-allyl)Pd(μ-*meso*DTO κ-*N*,*N* Pd κ-*S*,*S* M)$M(PR_3)Cl$] (**6**) are readily obtained. The connectivity of the binucleating ligand in the Pt−Pd heterobimetallic complex (**5**) has already been assessed in the parent compound [(η^3-allyl)-Pd(μ-{*s*,*S*}DTO) κ-*N*,*N* Pd κ-*S*,*S* Pt)Pt(PN)Cl];[2] the dithiooxamide bonds the palladium-allyl frame through the nitrogen atoms, and the Pt(PN)Cl moiety bonds through the sulfur chelating system. The palladium-allyl fragment is connected in a similar way to the $Pd(PR_3)Cl$ moiety in (**6**), as shown by a crystal structure determination (Figure 2). The structures of the bimetallic complexes were those expected; indeed the metal complexes [(H-*meso*DTO κ-*S*,*S* M)$M(PR_3)Cl$] (M = Pd, PR_3 = tri^{n}propyl-phosphine, M = Pt, and PR_3 = diphenyl-2-pyridyl-phosphine) can act as chelating ligands by means of the nitrogen chelating system of a κ-*S*,*S* M coordinated dithiooxamide. We therefore attempted to prepare the linkage isomer [[(η^3-allyl)Pd(μ-*meso*DTO κ-*S*,*S* Pd(allyl), κ-*N*,*N* $Pd(PR_3)Cl)Pd(PR_3)Cl$] by reacting [(η^3-allyl)Pd-(H-*meso*DTO κ-*S*,*S* Pd)] with a half-molar amount of [Pd(tri^{n}propyl-phosphine)$Cl_2]_2$. Unexpectedly, we obtained the same isomer as above, i.e., [(η^3-allyl)Pd(μ-*meso*DTO κ-*N*,*N* Pd(allyl), κ-*S*,*S* $Pd(PR_3)Cl)Pd(PR_3)$-Cl] (**6**).

Such a change in the coordination mode of the binucleating dithiooxamide is a probable consequence of the very high steric congestion between the N−$CH(CH_3)$-C_6H_5 group and the Pd-coordinated tri^{n}propyl-phosphane,

(33) Two types of chirality descriptors for metallocenic planar chirality can be found in the literature. The first is based on Schlögl's: Schlögl, K.; Fried, M. *Monatsh. Chem.* **1964**, *95*, 558–575. Schlögl, K.; Fried, M.; Falk, H. *Monatsh. Chem.* **1964**, *95*, 576–597. According to the Schlögl nomenclature, chirality descriptors are assigned depending upon either the clockwise (R) or anticlockwise (S) succession of ring substituents in order of decreasing priority with the shortest clockwise arc, as the molecule is observed from its principal axis perpendicular to the plane of the aromatic ligand with the π-bonded metal sitting underneath the plane. The second nomenclature proposed in 1967, once again by Schlögl, is an extension of the CIP system which was intended to replace the first nomenclature. In this system the metallocene ring carbon that bears the substitutent of highest priority is considered as a virtual sp^3 hybridized carbon, the ``planar chirality'' descriptor is obtained by applying the CIP sequence rule considering the π-bonded metal as being a substituent of this virtually tetrahedral carbon. This extended CIP system is used to assign either the pS or the pR stereochemical descriptor to planar chiral molecules, where the prefix ``p'' refers to the planar chiral character of the species. Readers are referred to the following reference for more details. Schlögl, K. *Top. Stereochem.* **1967**, *1*, 39–91. As in chiral plane-determined metal bound sp^2 carbons, one such carbon that bears the substituent of higher atomic number is considered as a virtual tetrahedral carbon, R and S descriptors can be used instead of pS and pR (ref 5a, p 1122).

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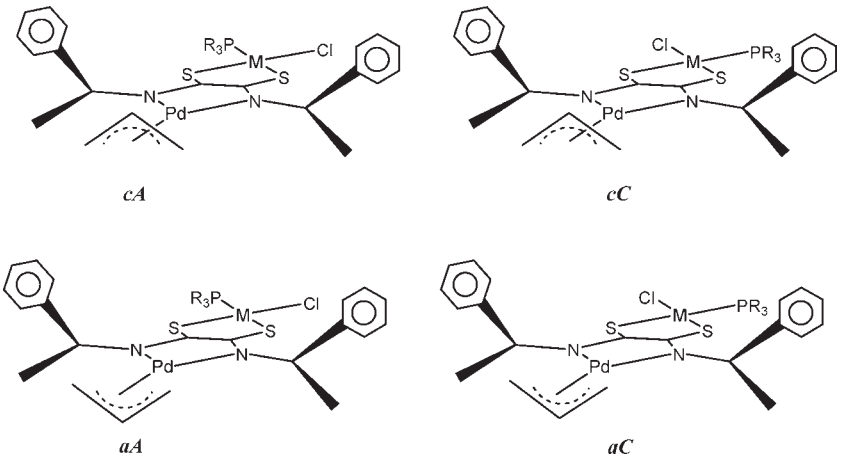
Chart 9. Molecular Structures of the Four Stereomers of the Complexes [(PR_3)ClM(*μ-meso*DTO *κ-S,S* M *κ-N,N* Pd)Pd(η^3-allyl)][a]



[a] (M = Pd, PR_3 = tri-^{n}propyl-phosphane, M = Pt, and PR_3 = diphenyl-2-pyridyl-phosphine) with the corresponding stereochemical descriptors.

which occurs when the metalloligand [(η^3-allyl)Pd(*μ-meso*DTO *κ-S,S* Pd] splits the chlorido-bridged dimer [Pd(tri^{n}propyl-phosphine)Cl_2]$_2$.

We have recently observed a similar rearrangement of the dithiooxamide ligand on converting the mononuclear metalloligand [(2-phenylpyridine *κ*-C,N Rh)Rh(H-diisoamyl-DTO *κ-S,S* Rh)] to the heterobimetallic derivatives [(2-phenylpyridine *κ*-C,N Rh)Rh(*μ*-diisoamyl-DTO *κ-N,N* Rh, *κ-S,S* M)ML_n] (ML_n = (η^3-allyl)Pd(II), (tri^n-propyl-phosphine)ClPd(II), (1,5-cyclooctadiene)Rh(I)).[44]

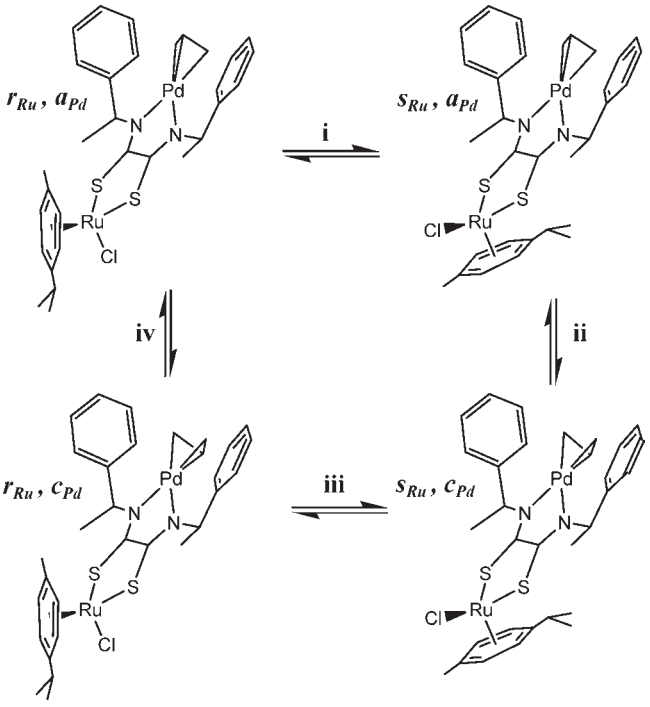
Regarding stereochemical features, the bimetallic complexes [[(η^3-allyl)Pd(*μ-meso*DTO *κ-N,N* Pd, *κ-S,S* M)M-(PR_3)Cl] contain two stereogenic elements, namely a pseudochiral palladium atom and a chiral [(*meso*DTO *κ-S,S* M) M (PR_3)Cl] plane. Thus, both Pd−Pd and Pd−Pt bimetallic complexes form enantiomeric pairs (Chart 9).

Accordingly, the NMR spectra of bimetallic complexes **6** and **7** show signals featuring an equimolar mixture of the two diastereomeric pairs. Furthermore, their bidimensional nuclear Overhauser enhancement spectroscopy (NOESY) spectra show spatial proximity between *syn*-allyl protons and methyl and phenyl groups of the dithioxamide ligand, and this supports the *κ-N,N* Pd-(allyl) coordination mode of the binucleating ligand.

The nuclear Overhauser effect (NOE) is observed between DTO hydrogens and *syn*-, but not *anti*-, allyl protons. Analogous selective NOEs for allyl derivatives have previously been reported by Pregosin et al. and have been attributed to CH syn twist toward the metal out of the allyl plane.[45]

NOESY spectrum of both **6** and **7** also show opposite phase cross peaks between allyl and DTO resonances of the two diastereomers, which constitute both of these two different bimetallic complexes. In particular, a syn−syn, anti−anti exchange has been observed. This clearly indicates that allyl pseudorotation occurs in solution, which interconverts the diastereomers into each other. The observed exchanges are consistent with a mechanism which involves: (a) dissociation of one Pd−N bond; (b) rotation around the remaining Pd−N bond; (c) isomerization of the T shaped intermediate; and (d) remaking of the Pd−N bond.[2]

Scheme 1. Equilibrium between the Four Isomers of **8** Due to Epimerization of Both Ru and Pd Centers



Finally, we combined a [(η^6-*p*-cymene)chlorido-ruthenium(II)] fragment with a [(η^3-allyl)palladium(II)] one by reacting the pseudochiral complex [(η^6-*p*-cymene)ClRu-(H-*meso*DTO *κ-S,S* Ru)] with a half-molar quantity of [(η^3-allyl)Cl_2Pd]$_2$.

In the resulting bimetallic complex [(η^6-*p*-cymene)-ClRu(*μ-meso*DTO *κ-S,S* Ru, *κ-N,N* Pd)Pd(η^3-allyl)Cl] (**8**) both ruthenium and palladium are pseudochiral centers. As a consequence, this complex should exist in four isomeric forms, which could be indicated by means of the descriptors proposed above for both pseudochiral mononuclear palladium and ruthenium.

The four isomers depicted in Scheme 1 are detectable in the ^{1}H and ^{13}C NMR spectra, as most of their chemical

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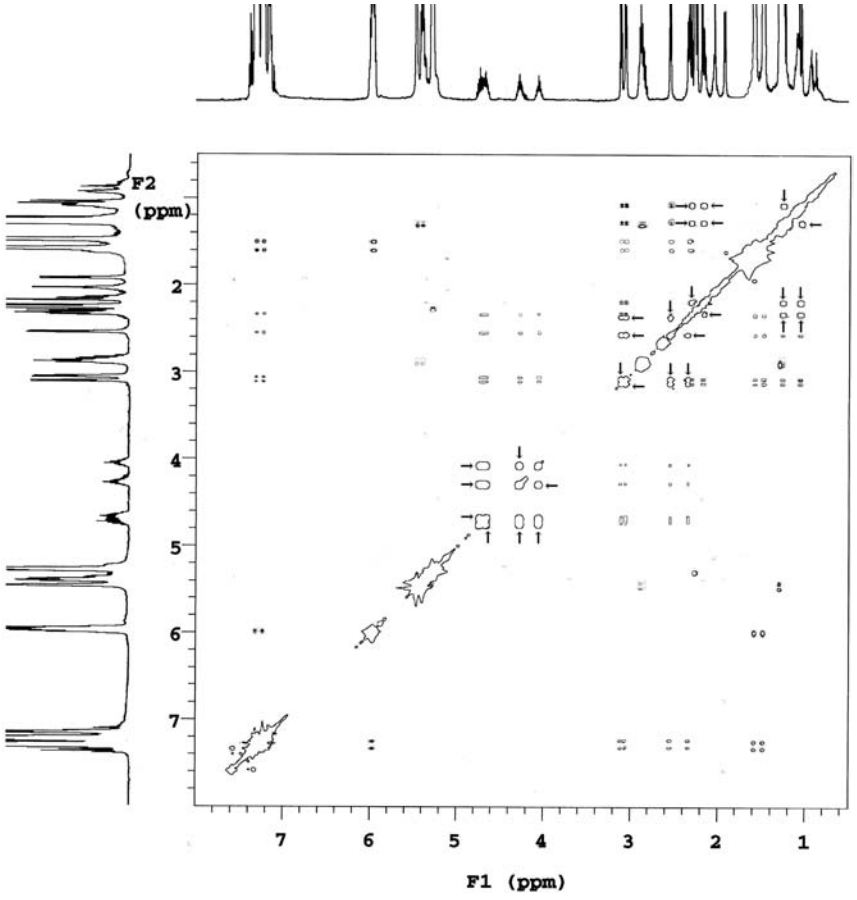


Figure 1. Phase-sensitive NOESY spectrum of [(η^6-*p*-cymene)ClRu(μ-*meso*DTO κ-*S*,*S* Ru, κ-*N*,*N* Pd)Pd(η^3-allyl)Cl] (**8**). Arrows indicate cross peaks which refer to the chemical exchange of central *syn*- and *anti*-allyl protons of the four isomers.

shifts differ from one another. One of these isomers was isolated as an X-ray quality crystal. The corresponding crystal structure, which is discussed below, shows the coordination mode of the binucleating ligand, which results κ-*S*,*S* Ru and κ -*N*,*N* Pd.

The NOESY spectrum of the four Pd−Ru isomers (Figure 1) also provides good evidence of such a coordination mode, since positive cross peaks occur between the methyl and phenyl protons of the DTO ligand and the *syn*-allyl protons.

Furthermore, in the above-described bidimensional spectrum, negative cross peaks between the four signals featuring the CH allyl proton as well as between the four *syn*-allyl doublets and between the four *anti*-allyl doublets are clearly distinguishable and prove the exchange of isomers due to the epimerization at both the palladium and ruthenium centers (Scheme 1).

We could infer that in the bimetallic complex [(η^6-*p*-cymene)ClRu(μ-*meso*DTO κ-*S*,*S* Ru, κ-*N*,*N* Pd)Pd(η^3-allyl)Cl] (**8**) both Ru−S and Pd−N bonds can break because of unfavorable hard−soft interactions[46] in κ-*S*, *S* Ru and κ-*N*,*N* Pd chelated moieties. As a consequence of the bond cleavage, inversion at palladium occurs through the above-mentioned allyl isomerization mechanism; in turn, the observed epimerization at the ruthenium center follows the Ru−S bond rupture.

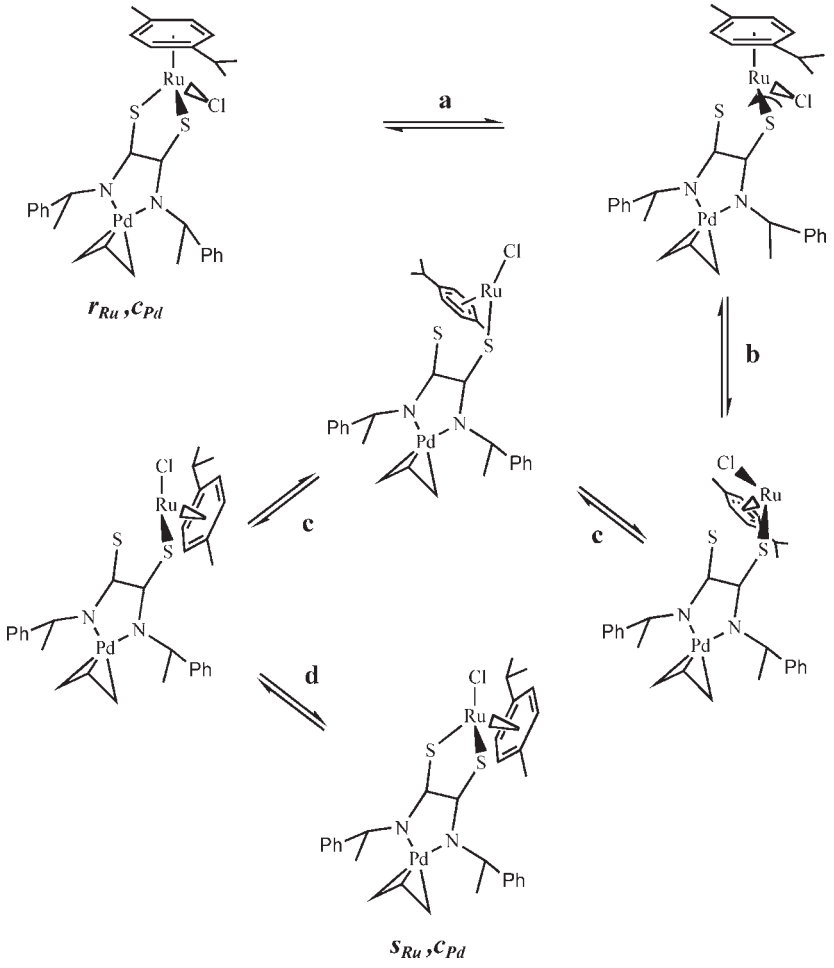
A mechanism which accounts for configurational inversion at the metal in chiral piano stool complexes has already been proposed by Brunner:[47] the M−halogen bond rupture provides a pyramidal intermediate with the same configuration as the starting material. The latter changes into a second pyramidal intermediate through a planar transition state, and finally the halogen ion restores the piano stool complex with the opposite configuration. Such a mechanism could also account for the epimerization process depicted in Scheme 1 (steps i and iii).

However, we have envisaged a slightly different mechanism for the epimerization process at our ruthenium pseudochiral center, since the low polarity of chloroform disfavors both the Ru−Cl rupture as well as the formation of ionic intermediates. Furthermore, the disfavored interaction between hard ruthenium and soft sulfur weakens the Ru−S bond; thus the rupture of one Ru−S bond produces a pyramidal intermediate which still has the configuration of the starting material (Scheme 2, step a). This pyramidal intermediate can rotate around the residual Ru−S bond (step b); therefore, a pyramidal intermediate with the opposite configuration can be produced through a planar transition state (step c), and the reforming of the Ru−S bond leads finally to the epimeric product (step d).[48]

(46) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539 and references therein.

(47) (a) Brunner, H.; Tsuno, T. *Acc. Chem. Res.* **2009**, *42*, 1501–1510. (b) Brunner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1194–1208.

Scheme 2. Proposed Mechanism for the Epimerization of the Pseudooctahedral Ruthenium in **8**[a]



[a] This mechanism refers to either steps i or iii in Scheme 1.

Crystal Structures. [(η^3-Allyl)(*c*)-Pd(μ-(*R*)1-(1-phenyl)-ethyl)-NSC−CSN-((*S*)-1-(1-phenyl)ethyl) κ-*N*,*N* (*c*)-Pd κ-*S*,*S* (*A*,*C*)-Pd)(*A*,*C*)-Pd(tri^{n}propyl-phosphine)Cl] (6). The asymmetric crystallographic unit of the complex (**6**) contains one discrete molecule showing chiral 1-phenylethyl groups of opposite configuration with respect to one another.

The crystal packing is centrosymmetric, and therefore, the crystallized compound is a racemic mixture of the two enantiomers *cC* and *cA*. The enantiomer with *cA* configuration is shown in Figure 2. The binucleating dithioxamide ligand shows the usual flat conformation generally observed in either *NN*,*SS* or *NS*,*NS* coordination mode;[1,2,4,42,44,48] its bond lengths (Table 1) are consistent with a single-bond character of the central C−C bond and the π-electron delocalization in both NCS frames.

The Pd_2 atom adopts a square planar geometry similar to that observed in an analogous Pd−Pt bimetallic complex.[2,49] Pd_1 coordination may be considered a distorted square planar geometry, since η^3-allyl behaves as a 'short bite' chelating ligand.

Interestingly, the allyl position appears perfectly defined and does not show any symmetrical split with respect to the coordination plane, as can be observed in other allyl−palladium complexes.[2,49,50] The allyl cuspid and the two phenyl rings of phenylethyl groups are oriented on opposite sides of the coordination plane. The (*S*)-1-(1-phenyl)ethyl group is on the right-hand side if one looks from the allyl CH toward the metal, and the absolute configuration of pseudoasymmetric palladium is therefore ***c***.

[(η^3-Allyl)(*c*)-Pd(μ-((*R*)-1-(1-phenyl)ethyl)-NSC−CNS-((*S*)-1-(1-phenyl)ethyl) κ-*N*,*N* (*c*)-Pd κ-*S*,*S* (*s*)-Ru)(*s*)-Ru(η^6-*p*-cymene)Cl] (8). Compound **8** crystallizes in the $P2_12_12_1$ space group. Phenyl rings of phenylethyl

(48) The proposed mechanism is only tentative and implies that other possible mechanisms could also account for the observed epimerization process. In particular, one of the referees observed that the similar rate at which both palladium and ruthenium centers epimerize does not match with an intramolecular mechanism such as the proposed one. Then he suggested that the initial Pd−N rupture in the symmetrical Pd−Ru bimetallic complex is followed by an intermolecular process of lower energy which causes the change in the ruthenium configuration. This is a very stimulating idea which, however, deserves further experimental evidence in support. In fact, we have preliminary results showing that the Ru(κ-*S*,*S* dithioxamide) chelate system is not very stable, and then we think that quantitative data are necessary in order to compare the stability of a Ru(κ-*S*,*S* dithioxamide) to a Pd(κ-*N*,*N* dithioxamide) interaction.

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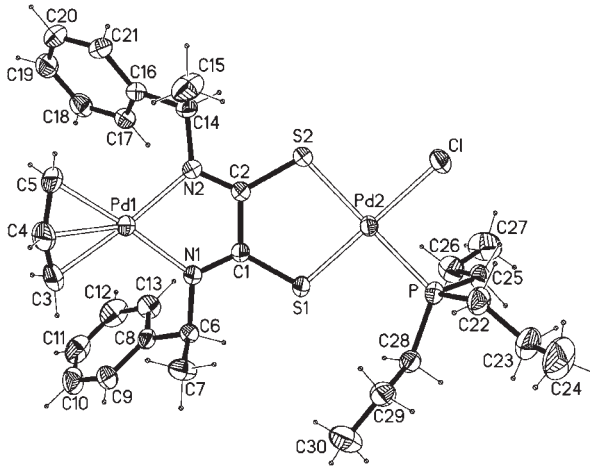

Figure 2. View of **6** in the asymmetric unit showing the numbering scheme. Thermal ellipsoids are drawn at 30% probability level, while hydrogen size is arbitrary.

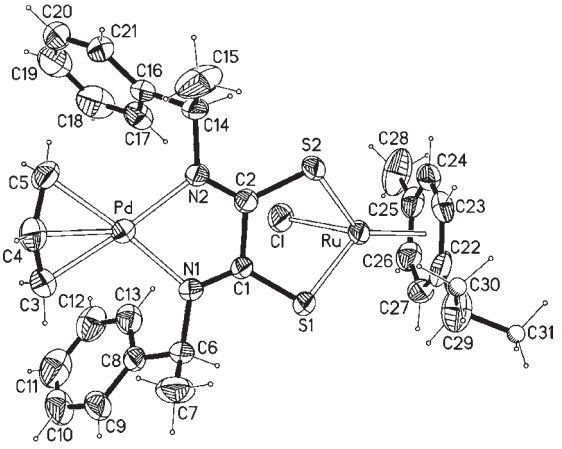

Figure 3. View of **8** with the numbering scheme used. Thermal ellipsoids are drawn at 30% probability level. Because of the rotational disorder of the isopropyl fragment, C_{30} and C_{31} atoms are represented by spheres of arbitrary size, as are the isotropic hydrogen atoms.

are oriented on opposite sides of the molecular plane with respect to the allyl cuspid but on the same side with respect to chlorine. Thus, the absolute configuration of palladium is *c* and that of ruthenium is *r*.

Bond distances and angles within the (μ-*meso*DTO κ-*S*,*S* Ru, κ-*N*,*N* Pd) fragment show the same values (within e. s.d.s) of the corresponding ones found in the compound bis-[(η^3-allyl)-palladium(II)](μ-bis-(*S*)-1-(1-phenyl)ethyl-dithiooxamidate-platinum(II) κ-*S*,*S* κ-*S*′,*S*′ Pt κ-*N*,*N* Pd κ-*N*′,*N*′ Pd′),[42] with the exception of the reciprocal differences in the helicity of phenylethyl groups.

The most important difference in the coordination array of the binucleating ligand in **8** (Figure 3) with respect to **6** is the change of dihedral angle between *S*,*S*, Ru and $S_2C_2N_2$ planes (10.49(6)° vs 34.11(7)°).

We have, in fact, always found that the binucleating dithiooxamide and the two metals in other bimetallic complexes are nearly coplanar.[1,2,4,42,44,49] However, we must take into account that the κ-*S*,*S* Ru (a hard−soft interaction) in this type of complex is unprecedented. Both S(1)-Ru and S(2)-Ru bond distances of 2.361(2) and 2.364(2) Å are comparable with those of other sulfur chelating ligands coordinated to Ru(II).[51] Weak hydrogen bonds involving chlorine and sulfur atoms, other than the usual van der Waals interactions, determinine the whole molecular packing.

Conclusion

In this paper we have synthesized and studied several new complexes containing paseudoasymmetric metal centers in either a symmetrical or a chiral environment. These metal centers change their configuration in accordance with a probable mechanism which implies the dissociation of both the Pt−N and Ru−S bonds. The pseudorotation of the allyl group around the palladium center is a well-established process, while the epimerization of a pseudo-octahedral ruthenium is still the subject of debate. Unlike organic chemistry, the knowledge of detailed mechanisms for configurational inversion in transition-metal chemistry is based on very few contributions.[52] Thus, any information regarding chiral-at-metal as well as pseudochiral-at-metal compounds are useful for the stereochemical analysis of transformations occurring in the coordination sphere of transition metals and especially in stereoselective catalysis processes.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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