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Trinuclear Heterobimetallic Complexes with Binucleating Dithioxamides: Stereoselective Synthesis and Solution Behavior Involving Pd–N Bond Rupture

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Bischelate platinum(II) complexes of the type [Pt(H–R_2–$N_2C_2S_2$)$_2$] (H–R_2–$N_2C_2S_2^-$ = dialkyl-dithioxamidate) are ditopic receptors which, after coordination of the first Pd(η^3-allyl)$^+$ moiety, induce the orientation of the second palladium–allyl fragment. Thus, a series of trimetallic complexes of formula bis-[(η^3-allyl)-palladium(II)](μ-bis-dialkyl-dithioxamidate-platinum(II) κ-*S*,*S*-κ-*S*′,*S*′-Pt-κ-*N*,*N*-Pd-κ-*N*′,*N*′-Pd′) has been prepared in which the allyl fragments are oriented toward the same side of the molecular plane. We have also prepared the trimetallic complex using a dithioxamide obtained from the racemic phenylethylamine. Only two isomers were produced in equimolar ratio: the racemate that has four homochiral alkyl substituents and the mesoform containing the *meso*-dithioxamide that has homochiral substituents on the same side of molecular plane. Under the effect of the temperature, the trimetallic Pd–Pt–Pd complexes undergo rapid allyl isomerization; the mechanism of the isomerization, which is similar to that found by us in an analogue Pt–Pd bimetallic complex, is discussed. The crystal and molecular structure of bis-[(η^3-allyl)-palladium(II)](μ-bis-{*S*}-phenylethyl-dithioxamidate-platinum(II) κ-*S*,*S*-κ-*S*′,*S*′-Pt-κ-*N*,*N*-Pd-κ-*N*′,*N*′-Pd′) has been reported.

Introduction

The use of complexes as ligands for step-by-step syntheses of polymetallic compounds is assuming increasing importance in modern inorganic chemistry.[1]

In particular, the sequential synthesis of linear metallic chains is a challenging issue because a linear array of metal atoms is viewed as a multicomponent molecular system which, depending on the properties of its individual components and on the mutual interactions between the various metal-based subunits, can exhibit interesting properties for topics such as catalysis, high performance materials, molecular sensory, and carriers in chemical and biological systems.[2]

Many efforts have been made to find binucleating ligands suitable for linking metal ions in successive steps; reliable approaches have exploited heterotopic ligands, which allow step-by-step syntheses because of different reactivity of the various chelating systems.

In this context, oxamato ligands have been extensively used to generate families of polymetallic compounds according to a sequential strategy;[3] however, the limitation of this generation of oxamato complexes was the isolation of solely heterobimetallic compounds. Notwithstanding this, properly designed oxamato ligands have overcome this inconvenience, and heterotrimetallic and heterotetrametallic complexes have recently been obtained.[4,5]

Another binucleating ligand, 1,10-phenanthroline-5,6-dione, has been used as a building block for polymetallic systems: it possesses a bifunctional character and exhibits different reactivity in its functionalities. This binucleating

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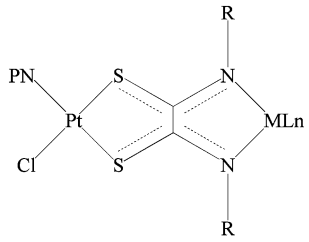
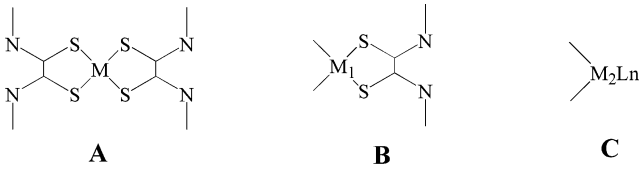
ligand has provided bi- and trimetallic derivatives, in some cases structurally characterized.[6−8]

In the past few years, we have found that platinum fragments linked to a deprotonated secondary dithioxamide through the sulfur-chelating system can function as a ligand complex: the ═N−H···N═ frame of the *S*,*S*-coordinated ligand is nucleophilic enough to split chloro-bridged dimers so that bimetallic complexes represented in the structure below (PN = diphenylphosphinopyridine; M = Pd or Ru; Ln = neutral or anionic ligands) are readily obtained.[9,109,10]

Following our previous results, we thought it would be



interesting to build up linear polymetallic chains through a modular use of bischelate dithioxamide complexes of the type $[M(HR_2DTO)_2]$ (M = divalent transition metal ions; R = alkyl groups) (A in the structure below), monochelate $[LnM_1(HR_2DTO)]$ precursors (B), and nonligating fragments coming from chloro-bridged dimers (C). In our perspective, A should be the bidirectional-growing module, B the monodirectional, and C the terminal one. Thus, we plan to build up the family of linear metallic chains $C-(B)_n-A-(B)_m-C$ ($0 \le n \le m$) because we have evidence that terminal group C can be sequentially introduced into the chains.



C-(B)$_n$-A-(B)$_m$-C

$0 \le n \le m$

The present paper describes a series of trimetallic complexes which can be viewed as the simplest members of the family ($n = m = 0$). They have been obtained by the reaction of $[Pt(HR_2DTO)_2]$ compounds (R = isopropyl, isoamyl, {*S*}-phenylethyl, racemic phenylethyl) with the palladium dimer $[(\eta^3\text{-allyl})PdCl]_2$.

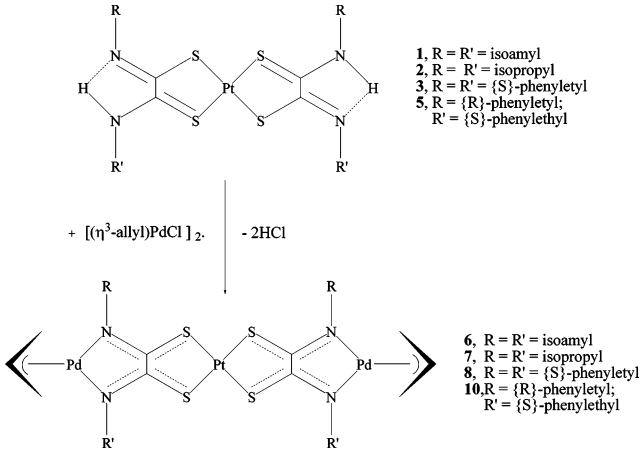
Several reasons led us to choose the allyl palladium derivatives: first, they play a prominent role as potential precursors or intermediates in several catalyzed organic syntheses;[11] furthermore, although a large number of allylpalladium complexes have been synthesized, their reactivity toward other metal derivatives has attracted somewhat less attention[12] despite the established value of bi- and polymetallic species as polyfunctional catalysts.[13]

Results and Discussion

Bischelate platinum(II) $[Pt(HR_2DTO)_2]$ species are readily obtained by the reaction of the 2-fold quantity of dithioxamide with *cis*-$Pt(Me_2SO)_2Cl_2$, followed by the dehydrohalogenation of the intermediate ion pair $\{(Pt(H_2R_2DTO)_2)^{+}\cdot 2Cl^{-}\}$.[14]

These species act as difunctionalized ligand complexes by means of the ═N−H···N═ frame of the *S*,*S*-coordinated dithioxamide, which, after the loss of residual amidic hydrogens, links two more metal fragments. Thus, we have reacted $[Pt(HR_2DTO)_2]$ species (R = isoamyl, isopropyl, {*S*}-1-phenylethyl, racemic 1-phenylethyl) with the stoichiometric quantity of $[(\eta^3\text{-allyl})PdCl]_2$.

The following process took place.



Trinuclear heterobimetallic complexes should exist as two diastereomeric forms: one having the two allyl moieties directed toward the same side of the molecular plane (endo isomer) and the other having allyl groups in opposite directions to one another (exo isomer).

An X-ray analysis performed on a single crystal of **8** revealed that the endo diastereomer was formed as the only product. ^1H, ^{13}C, and ^{195}Pt showed that also in solution there was only one diastereomer. We were able to demonstrate that the only compound detected in solution has the same

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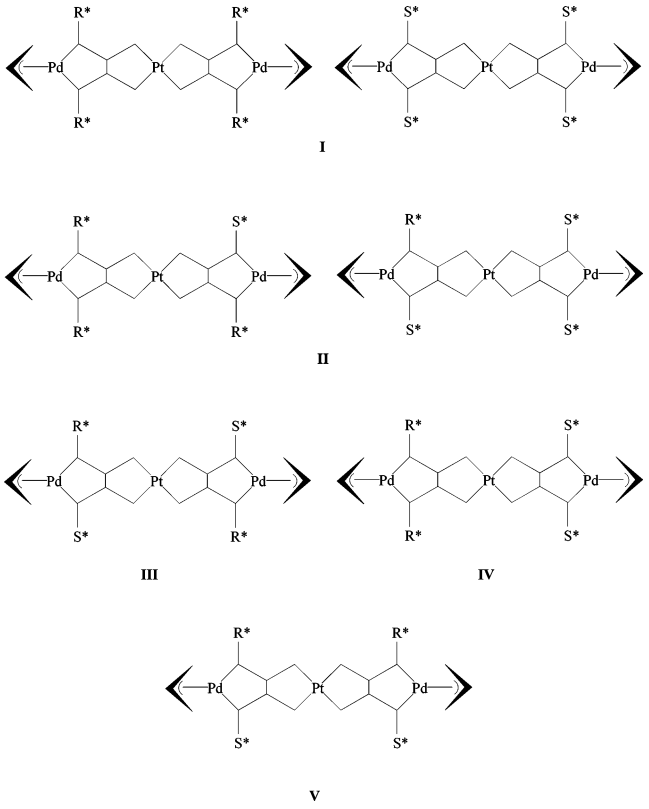
geometry observed in the solid state. For this purpose, we prepared compound **9** starting from an equimolar mixture of meso and racemic phenylethyldithioxamides. We would have expected **9** to be a mixture of five isomers in the following statistical ratio: 12.5 (racemate I):50 (racemate II):12.5 (mesoform III):12.5 (mesoform IV):12.5 (mesoform V). Very surprisingly, ^{1}H, ^{13}C, and ^{195}Pt NMR of **9** showed



only two sets of signals; one of them was identical to the signals of **8**, which is one of the two terms of racemate I. Hence, by subtracting the signals of the species **8** from the ^{1}H NMR spectrum of **9**, a spectral pattern remains which is compatible with the mesoform V. To further confirm the nature of the mixture **9**, we prepared the species **10** starting from the *meso*-phenlethyl-dithioxamide in a pure form. **10** was a pure product whose spectra were identical to the second set of signals detectable in the spectra of mixture **9**. (Figure 1).

In fact, isomers having chiral groups of opposite configuration on the same side of the molecular plane do not seem to have been formed. This is probably a stereomeric discrimination exerted by chiral substituents in the transition state preceding the stepwise formation of **5**.[15] Actually, it is possible to envisage two transition states leading to **5**; one of them shows the {*S*}-{*R*}···{*R*} interaction whose free energy might be more favorable with respect to that of the {*S*}-{*R*}···{*S*} interaction.

The stereochemical analysis of the species **10** confirms that trimetallic complexes exist in solution at room temperature as endo isomers. In fact, a compound having alkyl

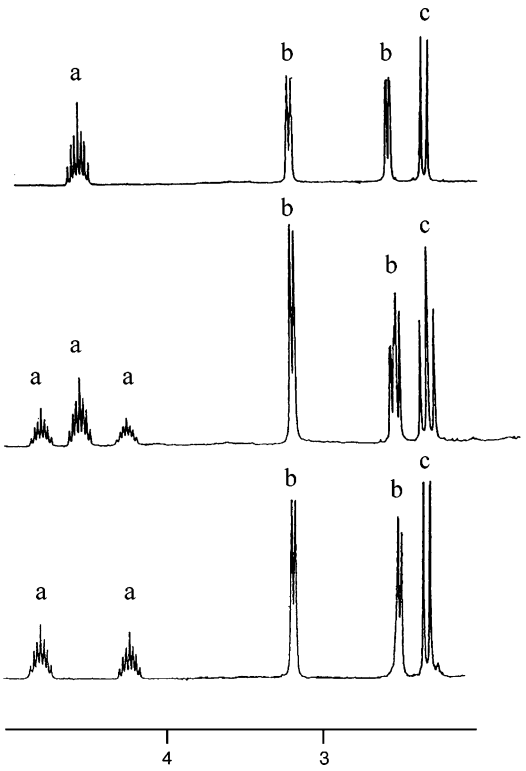


Figure 1. Allyl protons resonances of **8**, **9**, and **10**. Compound **9** is an equimolar mixture of **8** and **10** (a = central allyl protons; b = syn protons; c = low-field anti protons).

substituents placed as in V, but having allyl cuspids in direction opposite to one another, should have had C_{2h} symmetry and, consequently, should have shown only one set of signals for both allyl and alkyl groups.

This observed stereoselectivity is in contrast with that of other bis-allylpalladium complexes in which metals are connected by conjugated polydentate ligands with sp^2-hybridized nitrogen donors; these exhibit both isomers because of the two possible orientations of allyl cuspids.[16,17] However, a stereoselectivity similar to that observed by us was reported in a trimetallic complex where two allylpalladium moieties are connected by a difunctional (σ-alkynyl) platinum ligand complex.[18] These differences could be related to the extent of electronic communication between two metal centers M_1 linked by an organic binucleating ligand and by the influence of the presence of a metal fragment M_2 in a conjugated organic chain.[19]

In our opinion, once the first allylpalladium moiety enters the platinum precursor [Pt(HR$_2$DTO)$_2$], a back-donation mechanism correlates both palladium and platinum d orbitals through the NCS π-system of the binucleating ligand. Thus,

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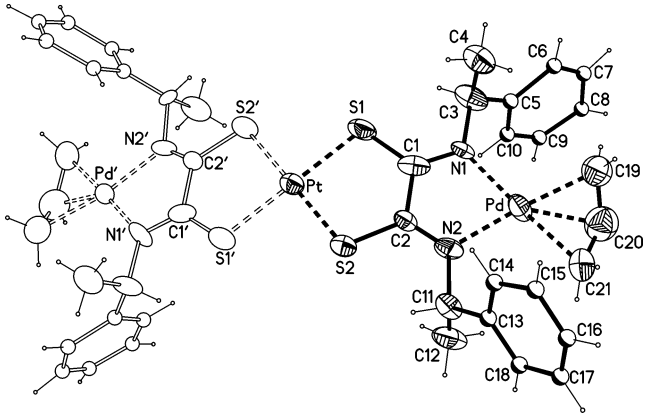

Figure 2. View of the asymmetric unit with atom-numbering scheme and thermal ellipsoids at 30% of probability, while H size is arbitrary. The empty atom andbonds represent the equivalent half-molecular unit obtained by the symmetry operation *y*, *x*, −*z*. The cocrystallized ethanol molecule is omitted for clarity. [Pt−S2 = 2.288(5), Pt−S1 = 2.301(5), Pd−N2 = 2.10(2), Pd−N1 = 2.11(2), Pd−C21 = 2.14(2), Pd−C19 = 2.15(2), Pd−C20 = 2.15(3), S1−C1 = 1.67(2), S2−C2 = 1.71(2), N1−C1 = 1.32(2), N2−C2 = 1.30(2), C1−C2 = 1.53(2) Å; S2′−Pt−S1 = 91.3(2), S2−Pt−S1 = 88.7(2), N2−Pd−N1 = 77.6(5), N2−Pd−C21 = 104.4(7), N1−Pd−C19 = 108.2(7), C21−Pd−C19 = 69.6(8)°].

the second palladium−allyl fragment will be forced to interact with the set of platinum d orbitals in a preferred orientation.

Crystal Structure of 8. The skeleton of **8** is characterized by three aligned square-planar d^8 metal atoms interconnected by two flat bischelate dithioxamidate bridges (Figure 2).

The molecule is chiral because of phenylethyl substituents of DTO. However, the crystal packing is also chiral because of the trigonal symmetry determined by the 3-fold screw axis. Co-crystallized solvent molecules, placed between adjacent trimetallic complexes, give rise to continuous "helicoidal ribbons" so that, in the solid state, **8** is constituted by infinite 3_1 helixes parallel to the *c* axis. The determined absolute configuration is the result of both the crystal arrangement (space group $P3_12$ vs its enantiomer $P3_22$) and the configuration of chiral substituents within the trimetallic molecule. The complex lies on a crystallographic two-fold axis passing through the platinum atom orthogonally to its coordination plane, and then the asymmetric unit contains only a half-molecular unit, with the two Pd fragments being equivalent. The complex exhibits a bent configuration as evidenced by the dihedral angle of 166.7(3)° between the Pt and Pd mean planes.

By considering the allyl a "short bite"-chelating ligand, the Pd coordination geometry might be considered a distorted square-planar with the allyl central C20 well located on one side of the coordination plane, while we have observed disordered configuration in analogous complexes with the central carbon split symmetrically on both sides.[10]

The Pt atom adopts a regular square-planar geometry similar to what we have already reported for the analogous bis-(di-*N*-butyldithioxamidato-*S*,*S*′)-platinum(II).[14] The same coordination of two similar chelating DTOs has been reported for bis-(di-*N*-benzyldithioxamidato-*S*,*S*′)-copper(II) where the distortion from the planarity is caused by the hindrance between the adjacent N−H of the ligands.[20]

Stereochemistry. The complexes **6** and **7** have C_{2v} symmetry because of the two internal reflection planes and the C_2 axis coinciding with their intersection. Because of the orientation of allyl groups, the molecular planes in **6** and in **7** are not symmetry planes; as a consequence, the geminal groups in alkyl substituents are diastereotopic and exhibit nondegenerate signals in the NMR spectra (ABC_2 spin system for $N-CH_2^-$ protons in **6**, R = isoamyl; two doublets featuring $N-C(CH_3)_2^-$ protons in **7**, R = isopropyl; two carbon resonances for geminal methyls, both in **6** and in **7**).

Compound **8** bears as alkyl substituents four identical homochiral groups; this causes the depletion of internal reflection planes, but not of the C_2 axis. As a consequence, in **8** atoms and atomic groups, which are not related by a 180° rotation around the C_2 axis, are diastereotopic. Thus, the ^{1}H NMR spectrum of **8** shows nondegenerate signals for both allyl prochiral hydrogens (two syn and two anti doublets) and chiral alkyl substituents (two partially superimposed quartets for methyns; two doublets for methyls). In addition, the ^{1}H NMR spectrum shows a further separation (2.1 and 1.7 Hz, respectively) between the doublets of allyl syn hydrogens and those of methyls in phenylethyl groups. Bidimensional COSY spectra and decoupling experiments showed that the observed separations, little but significant, are due to a ^4J coupling between syn allyl protons and an exceedingly long-range coupling (^7J) between methyne and methyl protons of the two phenylethyl group in the same dithioxamidate fragment.

Compound **10** is a mesoform having C_s symmetry. Being constituted by two diastereotopic halves, its ^{1}H NMR spectrum shows two equally intense sets of signals. The proton spectrum of **10** is not compatible with the C_{2v} symmetry of the mesoform III.

Solution Behavior and Isomerization Mechanism. Under the effect of temperature, compounds **6**−**10** undergo face-to-face isomerization of the allyl moieties. Changes in the spectra are described for achiral compounds **6** and **7**, for the enantiomerically pure complex **8**, and eventually for mesoform **10**.

Complexes 6−7. When the temperature rises, the ^{1}H NMR signals of geminal substituents in N−R groups collapse and, after coalescence, degenerate. In particular, ABC_2 resonances in **6** become an A_2B_2 spin system (Figure 3); the two methyl doublets of isopropyl groups in **7** become only one doublet at a high temperature. This happens because the metal plane in **6** and **7** becomes symmetrical as a consequence of the rapid allyl face exchange. Syn−anti proton exchange does not occur.

Complex 8. Methyls of phenylethyl groups collapse to only one doublet. The two syn and the two anti allyl doublets remain unchanged, but NOESY.tp spectra show that there is syn−syn/anti−anti exchange. These results are justified if one considers that two-time-averaged C_2 axes have to be added to the C_2 axis (perpendicular to them) existing also at

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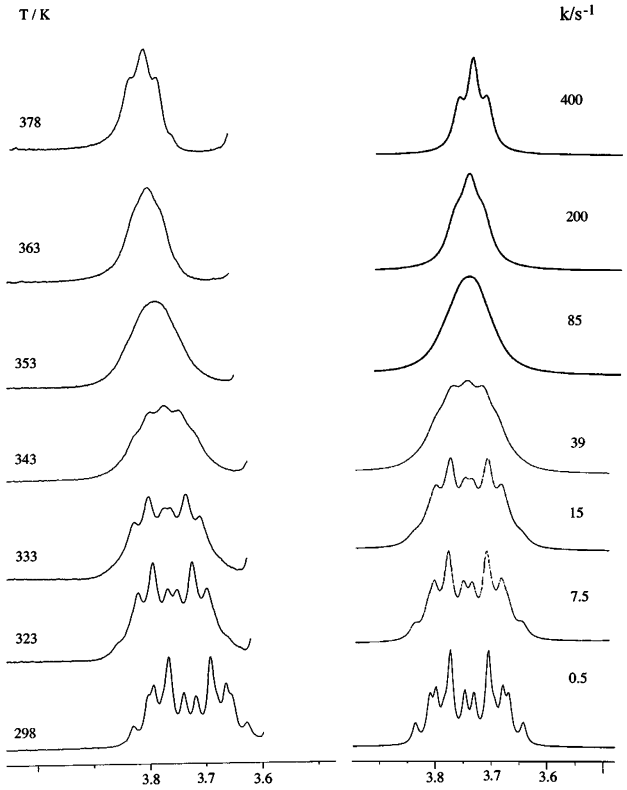

Figure 3. Selected variable-temperature spectra of [Pd(η^3-allyl)]$_2$\{μ-[(R$_2$-DTO)$_2$-Pt-κ-*S*,*S*-*S*′,*S*′-Pt,-κ-*N*,*N*-Pd,-κ-*N*′*N*′-Pd′] (R = isoamyl, **6**) in the region 3.6−3.9 ppm, solvent $CDCl_2CDCl_2$. Computer-simulated spectra are on the right.

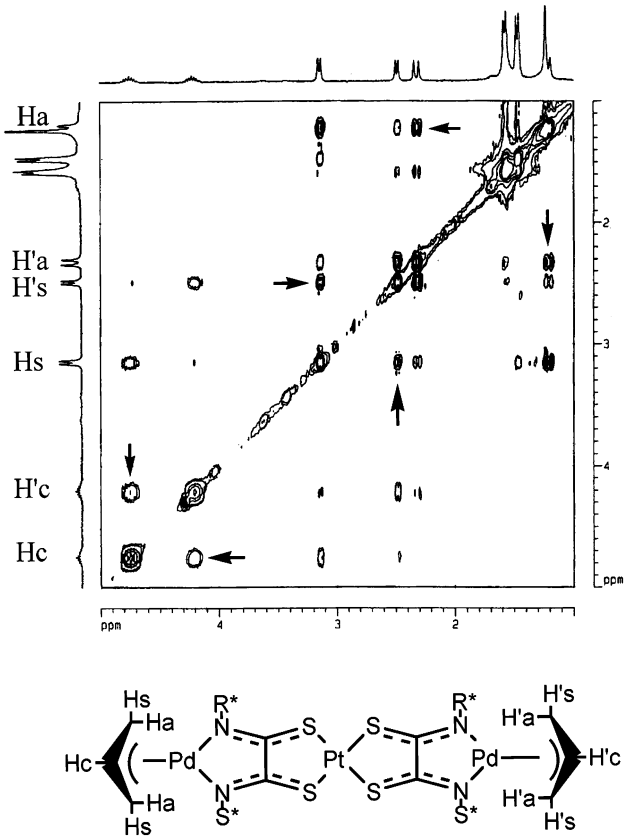

Figure 4. NOESY.tp spectrum of **10**. Arrows indicate positive cross-peaks, which refer to allyl protons exchange.

room temperature. The resonances of terminal allyl hydrogens remain asynchronous also at a high temperature because the time-average plane contains stereocenters.

Mesoform 10. The two multiplets of the central allyl CH under effect of temperature become two broad, unresolved signals and do not show further significant changes up to 390 K. Allyl signals (two syn doublets and two anti doublets) and $-CH_3$ phenylethyl signals (two doublets) are shifted in the spectrum until the temperature reaches 390 K. Higher temperatures do not produce further changes. Bidimensional NOESY.tp spectra (Figure 4) show exchange between the central allyl CH, as well as syn−syn/anti−anti exchange. At a high temperature, a time-averaged C_2 axis has to be added to the preexisting reflection plane (perpendicular to it); thus, the symmetry of the time-averaged molecule becomes higher. Nevertheless, both central and terminal allyl protons still show asynchronous NMR signals because the molecular plane contains stereocenters. Finally, in the ^{1}H NMR spectrum of **10**, no syn−anti exchange is observed.

The allyl isomerization, which is the source of the dynamic changes observed in solution, implies in all cases a syn−syn/anti−anti interchange. Although several mechanisms have been proposed, for this kind of interchange[21] some of these mechanisms are unlikely for our trimetallic complexes: (1) the $\eta^3-\eta^1$ isomerization can be discarded by the lack of syn−anti exchange, (2) the simple rotation of an allyl ligand, in its plane around an axis containing the metal center, is believed impossible in square-planar geometries,[21b] and (3) an associative mechanism, invoked by some authors[22] for this apparent allyl rotation, appears unlikely on the basis of the following NMR findings: (i) the solvent in our processes is chloroform or 1,2-dichloroethane, whose coordinating power is extremely low, and (ii) addition of methanol or acetone, as well as saturation with water, does not affect significantly the rate of the isomerization process. Furthermore, evidence against pentacoordinate pseudorotation arises from the lack of positive cross-peaks between the clearly resolved methyl resonances observed in the EXSY spectrum of the mononuclear complex (η^3-allyl)Pd({*S*}-((phenylethyl)$_2$-DTO) κ-*S*,*S*-Pd).[10] Presumably in this latter case the palladium−sulfur bonds, unlike the weaker Pd−N bonds of our trinuclear complexes, do not break, precluding the dissociative mechanism. The contemporary absence of syn−anti proton exchange for the latter complex further supports the hypothesis that high activation energy hinders allyl movements in these substances.

To obtain further information into the mechanism of the allyl isomerization, variable temperature ^{1}H NMR spectros-

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Table 1. Activation-Energy Data for the Allyl Isomerization Process in **6**, **7**, and **8**

compd	$\Delta G^{\ddagger}_{298K}$ (kJ mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1}mol^{-1})
6 R = isoamyl	74.6 ± 0.1	78.9 ± 1.2	14.3 ± 3.6
7 R = isopropyl	74.6 ± 0.3	80.6 ± 2.7	20.2 ± 8.1
8 R = {*S*}-phenylethyl	76.9 ± 0.1	81.5 ± 1.2	15.3 ± 3.7

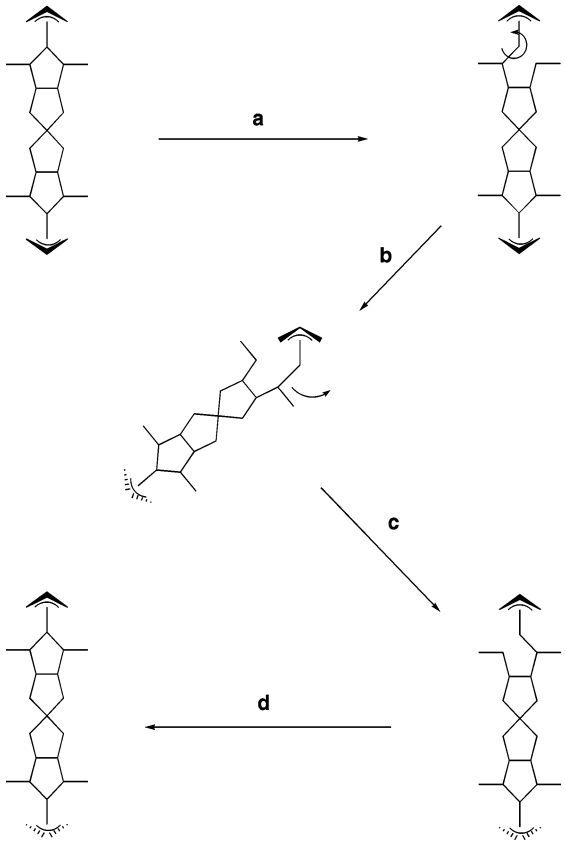
copy of the compounds was performed in $CDCl_2CDCl_2$ in the range 298−390 K, and simulations of the dynamic spectra were performed using the gNMR program. Because of the occurrence of some decomposition at a higher temperature, the activation-energy parameters (Table 1) were derived from the rate data in the temperature range 298−378 K (where the accuracy was greatest) and calculated from Eyring linear method. Some fittings for **6** are shown in Figure 3.

The chemical shifts of the geminal protons A, B (δ = 3.788 and 3.690, respectively) as well as the J_{AB} constant (11.10 Hz) and the coupling constant (7.70 Hz) with the methyl protons, not shown in the figure (δ = 1.47), were assigned in the static spectra with the help of decoupling experiments. On warming, the exchange A ⇄ B occurred, and the coalescence of their signals was observed around 353 K. At 378 K, the spectrum exhibited some exchange broadening, but at higher temperatures some decomposition precluded the calculation of the rate data. Thus, activation-energy data were calculated from 12 independent fittings in the temperature range shown. As is evident from Figure 4, the chemical shifts of A and B were temperature dependent. However, linear interpolation showed that $\delta_A - \delta_B$ was temperature independent, and no correction was made. Activation-energy data for the other complexes were obtained by a similar method and collected in Table 1.

Although the determination of $\Delta S^{\ddagger}$ values is based on extrapolation to $1/T = 0$ in the Eyring diagrams and, owing to the long distance over which this extrapolation has to be taken, is subject to some uncertainty, the data collected (Table 1) show that the activation entropies are, without doubt, positive. Thus, the transition-state conformations should be sterically less congested than the ground-state conformations, indicating that an associative mechanism can be discarded. Furthermore, the $\Delta S^{\ddagger}_{298K}$ values for the present complexes and the species [(PN)ClPt(μ-$R_2N_2S_2C_2$-κ-*S*,*S*-Pt-κ-*N*,*N*-Pd)Pd(η^3-C_3H_5)][10] are of comparable magnitude, strongly suggesting that a similar mechanism is operative.

The only mechanism consistent with all the experimental results appears to be a dissociative mechanism, reported by other authors[15,23] and by ourselves[10] for palladium−allyl complexes with N-donor ligands. Thus, we suggest a mechanism that involves, in each allyl fragment, (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 (steps b and c may be inverted; see Scheme 1).

Scheme 1



Experimental Section

Dithioxamide ligands (H_2R_2DTO) (R = isoamyl, isopropyl, {*S*}-1-phenylethyl) were synthesized according to Hurd.[24] ({*R*}-1-Phenylethyl-{*S*}-1-phenylethyl)DTO (*meso*-DTO) was obtained by fractionary crystallization from ethanol of an equimolar mixture of *meso*- and *rac*-DTO synthesized starting from racemic 1-phenylethyl-amine. The complex $Pt(DMSO)_2Cl_2$ was prepared according to Kukushkin.[25] Other reagents were commercially available products used as purchased. Solvents were freshly distilled from sodium wire under a nitrogen atmosphere. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 298 K on a Bruker ARX-300 spectrometer equipped with a broad-band probe operating at 300.13 and 75.46 MHz, respectively [δ (ppm) relative to Me_4Si, J (Hz)]. Variable-temperature ^{1}H NMR spectra of the compounds were obtained in $CDCl_2CDCl_2$ in the range 298−380 K. Because of the occurrence of some decomposition at higher temperature, the calculated activation energy was based on fittings of experimental spectra in the temperature range 298−363 K (where the accuracy was greatest). Simulation of the dynamic spectra was performed using the gNMR program.[26] The activation-energy data were calculated from Eyring linear method and are listed in Table 1.

General Procedure for the Synthesis of the Bis-dithioxamidato Complexes [Pt(HR_2DTO)$_2$] (R = isoamyl, **1**; isopropyl, **2**; {*S*}-phenylethyl, **3**; meso and racemic phenylethyl, **4**; *meso*-phenylethyl, **5**)**:** To a stirred suspension of *cis*-Pt $(Me_2SO)_2Cl_2$ (211 mg, 0.5 mmol) in chloroform (60 mL) was added H_2R_2DTO (1

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mmol). The reaction went to completion within 0.5 h at room temperature, and the solution turned purple. A 200 mg sample of sodium bicarbonate was added, and the solution turned yellow. After 0.5 h of stirring, the solution was filtered and concentrated to a small volume (∼10 mL). The solid obtained by addition of petroleum ether 40−60 (∼100 mL) was collected and washed with diethyl ether.

(1): ^{1}H NMR ($CDCl_3$): $\delta = 3.16$ (t, $^3J = 6.20$ Hz, 8 H, N−CH_2), 1.65 [m, 12 H, N−CH_2−CH_2−CH(CH_3)$_2$], 0.92 (d, $^3J = 6.20$ Hz, 24 H, CH_3). ^{13}C NMR: $\delta = 179.43$ (CS), 47.78 (N−CH_2), 37.50 (N−CH_2−CH_2), 26.25 (CH), 22.40 (CH_3). Anal. Calcd for $C_{24}H_{46}N_4PtS_4$: C, 40.37; H, 6.49; N, 7.85. Found: C, 40.45; H, 6.60; N 7.80. Yield 91%.

(2): ^{1}H NMR ($CDCl_3$): $\delta = 4.28$ (sl, $^3J = 6.40$ Hz, 4 H, CH), 1.30 (d, 24 H, CH_3). ^{13}C NMR: $\delta = 178.1$ (CS), 50.4 (CH), 21.7 (CH_3). Anal. Calcd for $C_{16}H_{30}N_4PtS_4$: C, 31.94; H, 5.02; N, 9.31. Found: C, 31.95; H, 5.10; N, 9.25. Yield 90%.

(3): ^{1}H NMR ($CDCl_3$): $\delta = 7.37-7.18$ (m, 24 H, Ph) 5.30 (q, $^3J = 6.63$ Hz, 4 H, N−CH), 1.60 (d, 12 H, CH_3). ^{13}C NMR: $\delta =$ 179.30 (CS), 142.3 (q-Ph), 129−126.5 (*o*,*m*,*p*-Ph), 58.05 (N−CH), 21.35 (CH_3). Anal. Calcd for $C_{36}H_{38}N_4PtS_4$: C, 50.87; H, 4.50; N 6.59. Found: C, 50.80; H, 4.65; N, 6.65. Yield 92%.

(4): Anal. Calcd for $C_{36}H_{38}N_4PtS_4$: C, 50.87; H, 4.50; N, 6.59. Found: C, 50.90; H, 4.65; N, 6.60. Yield 89%.

(5): ^{1}H NMR ($CDCl_3$): $\delta = 7.37-7.18$ (m, 24 H, Ph), 5.27 (q, $^3J = 6.63$ Hz; 4H, N−CH), 1.62 (d, $^3J = 6.63$ Hz, 12 H, CH_3). ^{13}C NMR: $\delta = 179.27$ (CS), 179.20 (CS), 142.1 (q-Ph), 128.75 (*o*-Ph), 128.70 (*o*-Ph), 127.6 (*p*-Ph), 127.5 (*p*-Ph), 126.55 (*m*-Ph), 126.35 (*m*-Ph), 58.05 (N−CH), 21.35 (CH_3), 21.30 (CH_3). Anal. Calcd for $C_{36}H_{38}N_4PtS_4$: C, 50.87; H, 4.50; N, 6.59. Found: C, 50.72; H, 4.63; N, 6.56. Yield 90%.

General Procedure for the Synthesis of the Trinuclear Complexes Bis-[(η^3-allyl)palladium(II)](μ-bis-dialkyl-dithioxamidate-platinum DTO-κ-*S*,*S*-κ-*S*′,*S*′-Pt-κ-*N*,*N*-Pd-κ-*N*′,*N*′-Pd′) (R = isoamyl, **6**; isopropyl, **7**; {*S*}-phenylethyl, **8**; meso and racemic phenylethyl, **9**; *meso*-phenylethyl, **10):** 1 mmol of [Pd(η^3-allyl)(μ-Cl)]$_2$ was dissolved in chloroform (∼40 mL), and 1 mmol of [Pt-($HR_2DTO)_2$] was added. The stirred solution turned red, and after 2 h it was concentrated to a small volume (∼10 mL). By adding petroleum ether 40−60 (∼100 mL), red-orange trimetallic complex was obtained. No byproducts were obtained.

(6): ^{1}H NMR ($CDCl_3$): $\delta = 5.46$ (m, 2 H, allyl CH), 3.84 (dt, $^2J = 11.1$ Hz, $^3J = 7.7$ Hz, 4 H, N−CH_2), 3.73 dt, $^2J = 11.1$ Hz, $^3J = 7.7$ Hz, 4 H, N−CH_2), 3.55 (d, $^3J = 7.0$ Hz, 4 H, syn allyl), 2.94 (d, $^3J = 12.5$ Hz, 4 H, anti allyl), 1.58 (m, 12 H, N−CH_2−CH_2−CH), 0.95 (d, $^3J = 6.25$ Hz, 24 H, CH_3). ^{13}C NMR: $\delta =$ 191.0 (*C*S), 115.2 (CH allyl), 57.6 (CH_2 allyl), 57.2 (N−CH_2), 36.8 (N−CH_2−CH_2), 26.6 (N−CH_2−CH_2−*C*H), 22.8 (CH_3), 22.7 (CH_3). Anal. Calcd for $C_{30}H_{54}N_4Pd_2PtS_4$: C, 35.78; H, 5.78; N, 5.56. Found: C, 35.80; H, 5.60; N, 5.50. Yield 75%.

(7): ^{1}H NMR ($CDCl_3$): $\delta = 5.26$ (m, 2H, CH allyl), 4.64 (sl, $^3J = 6.4$ Hz, 4 H, N−CH), 4.12 (d, $^3J = 6.7$ Hz, 8 H, syn allyl), 2.89 (d, $^3J = 12.5$ Hz, 8 H, anti allyl), 1.14 (d, 12 H, $^3J = 6.4$ Hz, CH_3) 1.04; (d, 12 H, $^3J = 6.4$ Hz, CH_3). ^{13}C NMR: $\delta = 189$ (CS), 111.5 (CH allyl), 57.22 (CH_2 allyl), 55.02 (N−CH), 27.22 (CH_3), 21.86 (CH_3). Anal. Calcd for $C_{22}H_{38}N_4Pd_2PtS_4$: C, 29.53; H, 4.28; N, 6.26. Found. C, 29.50; H, 4.35; N, 6.20. Yield 73%.

(8): ^{1}H NMR ($CDCl_3$) $\delta = 7.32-7.16$ (m, 20 H, Ph protons), 5.80 (q, $^3J = 6.6$ Hz, 2 H, N−CH), 4.50 (m, 2 H, CH allyl), 3.14 (d, $^3J = 7.0$ Hz; 2 H, syn allyl), 2.51 (dd, $^3J = 7.0$ Hz; ^4J syn = 2.1, 2 H, syn allyl), 2.26 (d, $^3J = 12.6$ Hz, 2 H, anti allyl), 1.57 (dd, $^3J = 6.6$ Hz, $^7J = 1.6$ Hz, 6 H, CH_3), 1.48 (dd, $^3J = 6.6$ Hz, $^7J = 1.6$ Hz, 6 H, CH_3), 1.34 (d, $^3J = 12.6$ Hz, 2 H, anti allyl). ^{13}C NMR: $\delta = 190.40$ (s, CS), 190.10 (s, CS), 143.20 (q-Ph), 142.30 (q-Ph), 128−126.6 (*o*,*m*,*p*-Ph), 111.65 (CH allyl), 60.82 (s, N−CH), 58.17 (CH_2 allyl), 57.66 (CH_2 allyl), 18.38 (CH_3), 17.43 (CH_3). ^{195}Pt NMR: $\delta = 361.00$. Anal. Calcd for $C_{42}H_{46}N_4Pd_2PtS_4$: C, 46.23; H, 4.25; N, 5.13. Found: C, 46.40; H, 4.35; N, 5.20. Yield 75%.

(9): Anal. Calcd for $C_{42}H_{46}N_4Pd_2PtS_4$: C, 46.23; H, 4.25; N, 5.13. Found: C, 46.33; H, 4.385; N, 5.15. Yield 71%

(10): ^{1}H NMR ($CDCl_3$): $\delta = 7.32-7.16$ (m, 20 H, Ph protons), 5.77 (q, $^3J = 6.5$ Hz, 2 H, N−CH, 4.74 (m, 1 H, CH allyl), 4.19 (m, 1 H, CH allyl), 3.14 (d, $^3J = 7.2$ Hz, 2 H, syn allyl), 2.47 (d, $^3J = 7.2$ Hz, 2 H, syn allyl), 2.31 (d, $^3J = 12.3$ Hz, 2 H, anti allyl), 1.56 (dd, $^3J = 5.5$ Hz, $^8J = 1.6$ Hz, 6 H, CH_3), 1.19 (d, $^3J = 12.3$ Hz, 2 H, anti allyl). ^{13}C NMR: $\delta = 190.4$ (CS), 143.25 (q-Ph), 128.80−126.50 (*o*,*m*,*p*-Ph); 112.50 (CH allyl), 110.50 (CH allyl), 60.82 (s, N−CH), 57.74 (CH_2 allyl), 18.00 (CH_3), 17.10 (CH_3). ^{195}Pt NMR: $\delta = 360.3$. Anal. Calcd for $C_{42}H_{46}N_4Pd_2PtS_4$: C, 46.23; H, 4.25; N, 5.13. Found: C, 46.30; H, 4.35; N, 5.10. Yield 67%.

X-ray Crystallographic Studies of 8. Crystal data: $C_{44}H_{52}N_4OPd_2PtS_4$, fw = 1189.03, trigonal space group $P3_12$, $a = 11.076(2)$, $c = 32.283(7)$ Å, $V = 3430$ (1) Å^3, $Z = 3$, $F(000) = 1758$, $D_c = 1.727$ g/cm^3, $\lambda =$ Mo Kα (0.71073 Å), $\mu = 40.50$ cm^{-1}.

Diffraction data of a $0.30 \times 0.22 \times 0.20$ mm^3 orange-red crystal were collected at room temperature on a Siemens P*4* automatic four-circle diffractometer by using a graphite monochromated Mo Kα radiation. Lattice parameters were obtained from least-squares refinement of the setting angles of 35 reflections with $11° \le 2\theta \le 30°$. The reflection intensities, collected up to $2\theta = 53°$ by fixed-speed $\omega-2\theta$ scan technique, were evaluated by a profile fitting of the 2θ shell procedure[27] and then corrected for Lorentz polarization effects. No crystal decay was observed. An absorption correction was applied by fitting a pseudoellipsoid to the azimuthal scan data of 12 high χ reflections.[28] No account was taken for extinction effects. Data reduction has been performed by SHELXTL-PLUS system.[29]

The data set analysis pointed to the enantiomorphous $P3_22$ and $P3_12$ space groups, and at the beginning, the first one was arbitrarily chosen. The crystal structure was solved by standard Patterson method and subsequently completed by a combination of least-squares technique and Fourier syntheses. H atoms, except the ethanol hydrogens, were included in the refinement among the "riding model" method with the X−H bond geometry and the isotropic displacement parameter depending on the parent atom X. The refinement, with all nonhydrogen atoms anisotropic and minimizing the function $\sum w(F_o^2 - F_c^2)^2$, was carried out by the full matrix least-squares technique, based on all independent 1471 F^2, with SHELXL97.[30] The co-crystallized ethanol solvent appeared very disordered, and only one clear arrangement was revealed on a two-fold axis with the oxygen atom equally distributed in two equivalent positions. The last model refinement cycles were performed in both the acentric packings, and $P3_12$ gave the best results as confirmed by the enantiomorphic parameter that converged to −0.04(2) close to the expected 0 value of the right absolute configuration.[31] The model converged to the final residual R1(*obs*/*all*) = 0.042/0.092, *w*R2(*obs*/*all*) = 0.090/0.098 (where *obs* = 777 reflections with $I \ge 2\sigma(I)$) and goodness-of-fit = 0.803. In

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the last difference Fourier map, the significant density residuals were up to 0.8 e $Å^{-3}$ within 1 Å from the metal atoms.

Final geometrical calculations and drawings were carried out with the PARST program[32] and the XP utility of the Siemens package, respectively.

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Supporting Information Available: Tables of crystallographic data and data collection details, atomic coordinates, thermal displacement parameters, bond lengths and angles, hydrogen atom coordinates, torsion angles, and crystal packing picture for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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