Synthesis, Stereochemistry, and Solution Dynamics of Heterobimetallic Complexes with Metals Connected by Dithioxamides in κ-S,S′ κ-N,N′ Binucleation Mode. The Molecular Structure of [2-(Diphenylphosphino)pyridine-Pt-Cl-(μ-*N*,*N*′-dibenzyldithioxbisamidato-κ-*S*,*S*′-Pt-κ-*N*,*N*′-Pd)(η³-allyl)Pd]

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Dehydrohalogenation of dithioxamide complexes $\{(PN)ClPt(H_2R_2N_2C_2S_2)^+(Cl^-)\}$ (PN = 2-(diphenylphosphino)pyridine; $H_2R_2N_2C_2S_2$ = secondary dithioxamides, H_2DTO, R = ethyl, **1**; R = benzyl, **2**; R = {*S*}-phenylethyl, **3**) leads to the dithioxamidates $[(PN)Cl]Pt(HR_2N_2C_2S_2)]$ ($HR_2N_2C_2S_2^-$ = dialkyldithioxamidate, HDTO) **4**−**6**, which can act as ligands (*complexes as ligands*). In fact, after deprotonation, they can easily promote chloro-bridge splitting reaction of $[Pd(\eta^3\text{-allyl})(\mu\text{-Cl})]_2$ leading to heterobimetallic complexes of formula $[(PN)ClPt(\mu\text{-}R_2N_2C_2S_2\text{-}\kappa\text{-}S,S\text{-Pt-}\kappa\text{-}N,N\text{-Pd})Pd(\eta^3\text{-allyl})]$; $R_2N_2C_2S_2^{2-}$ = dialkyldithioxbisamidate, DTO; R = ethyl, **7**; R = benzyl, **8**; R = {*S*}-phenylethyl, **9**. These complexes are chiral; hence, **7** and **8** have been synthesized as racemates, and **9** as an equimolar diastereomeric mixture owing to the optically pure {*S*}-phenylethyl substituent. Upon warming, **7** and **8** racemize, and **9** epimerizes. The isomerization processes may be explained by a mechanism that involves (a) breaking of one of the two Pd−N bonds; (b) rotation around the remaining Pd−N bond; (c) isomerization of the T-shaped intermediate; and (d) remaking of the Pd−N bond. The solid structure of complex **8** has been determined by X-ray single-crystal diffraction analysis.

Introduction

Secondary dithioxamides are "exotic" ligands, for both their versatility and multisite donor nature. Their coordination chemistry is further complicated by the fact that these ligands acting as neutral, monoanionic, or dianionic species display rather flexible metal−ion binding patterns.

Even though in neutral or monoanionic form dithioxamides generally chelate a single metal through sulfur atoms,[1] several examples of trans-S,S′ binucleation,[2] S-monocoordination,[3] and NS−N′S′ "exo" binucleation[4] have been reported. In turn, a dianionic rubeanate $R_2N_2C_2S_2^{2-}$ generally gives rise to oligonuclear or polymeric systems in which the ligand coordinates metals in an NS′−N′S binucleation mode.[5] To the best of our knowledge only one report has appeared concerning dithioxamides in N,N′ cis-chelation mode,[6] whereby it deals with a trimetallic copper complex in which the unusual coordination mode is reached owing to particular steric requirements of the dithioxamidic ligand.

By reacting a Pt^{II} ligand complex containing an S,S′-chelated dithioxamide with a ruthenium *p*-cymene dichloro dimer, we have recently obtained a binuclear Pt−Ru complex with the metals connected by means of a dithioxamide ligand in a κ-S,S′ Pt κ-N,N′ Ru coordination mode.[7] This binuclear complex shows intrinsic interest because it presents a unique example of a bimetallic chiral axis. Its synthetic procedure is however also interesting since it deals with an S,S′-coordinated dithioxamide that is forced to link a second metal in an N,N′-cis-coordination mode. In other words, the synthesis of the referred bimetallic complexes has been achieved according to the procedure of "complexes as ligands".

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(1) Antolini, L.; Fabretti, A. C.; Franchini, G.; Menabue, L.; Pellacani, G. C.; Desseyn, H. O.; Dommisse, R.; Hofmans, H. C. *J. Chem. Soc., Dalton Trans.* **1987**, 1921. Desseyn, H. O.; Van deer Veken, B. J.; Hermann, M. A. *Appl. Spectrosc.* ***1978***, *32*, 101. Rosace, G.; Bruno, G.; Scolaro, M. L.; Nicolò, F.; Sergi, S.; Lanza, S. *Inorg. Chim. Acta* **1993**, *39*, 208.

(2) (a) Drew, M. G. B.; Kisenyi, J. M.; Willey, G. R.; Wandiga, S. O. *J. Chem. Soc., Dalton Trans.* **1984**, 1717. (b) Baggio, R.; Garland. M. T.; Perec, M. *J. Chem. Soc., Dalton Trans.* **1995**, 987.

(3) Belicchi Ferrari, M.; Gasparri Fava, G.; Pelizzi, C.; Tarasconi, P. *Inorg. Chim. Acta* **1985**, *98*, L49.

(4) Girerd, J. J.; Jeannin, S.; Jeannin, Y.; Kahn, O. *Inorg. Chem.* **1978**, *17*, 3034.

(5) (a) Veit, R.; Girerd, J. J.; Kahn, O.; Robert, F.; Jeanin, Y.; El Murr, N. *Inorg. Chem.* **1984**, *23*, 4448. (b) Ye, Q. Y.; Nakano, Y.; Frauenhoff, G. R.; Whitcomb, D. R.; Tagusakawa, F.; Bush, D. H. *Inorg. Chem.* **1991**, *30*, 1503.

(6) Veit, R.; Girerd, J. J.; Kahn, O.; Robert, F.; Jeannin, Y. *Inorg. Chem.* **1986**, *25*, 4175; Journaux, Y.; Lloret, F.; Kahn, O. *Inorg. Chem.* **1990**, *29*, 3048.

(7) Lanza, S.; Bruno, G.; Nicolò, F.; Scopelliti, R. *Tetrahedron, Asymmetry* **1996**, *7*, 3347.

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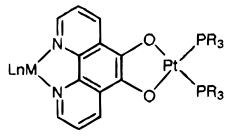
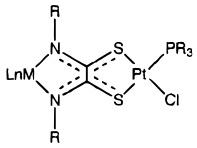
This procedure to synthesize polymetallic complexes is becoming more and more popular, but only a few systematic syntheses have been to date described. One of them, perhaps the most successful, exploits binucleating ligands having equivalent coordination sites such as bipyrimidine and related ligands.[8] Another promising procedure is based on coordinating properties of dipyridilcatecolate (dpcat), which was detected by Balch as a "dual chelating ligand" in 1975.[9] Using dpcat as a dual ligand, Pierpoint obtained a bimetallic complex[10] whose structure is similar to that of a Pt−Ru complex recently reported by some of us[7] and to the binuclear species **7**, **8**, and **9** described in this paper.



(I)

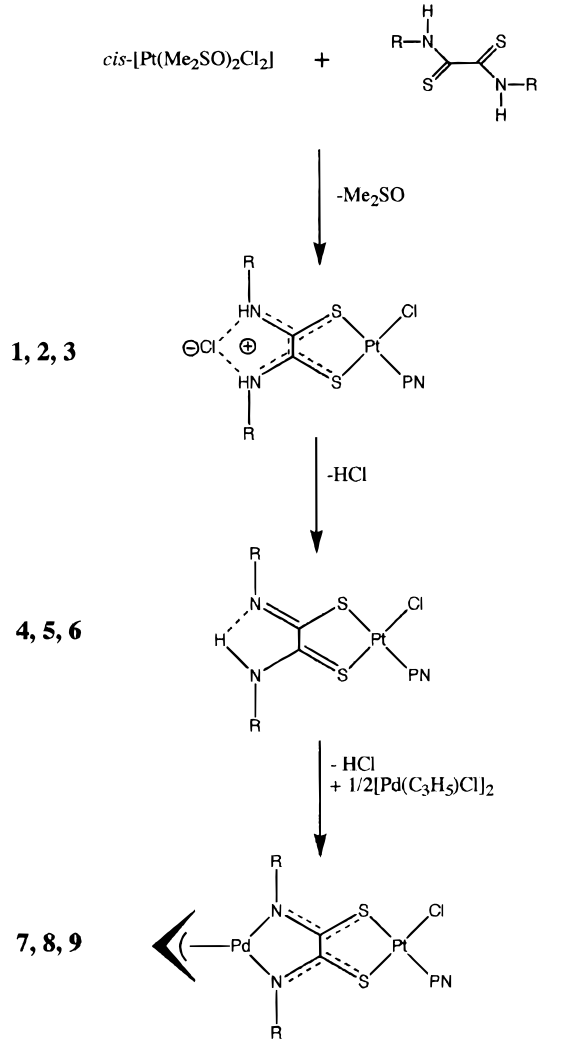


(II)

Pierpoint's synthetic procedure seems to be of general applicability and has been recently exploited by authors interested in electrochemical[11] and photochemical[12] aspects of heterobimetallic complexes. Furthermore, the formation of bi- and trimetallic complexes having dpcat as the bridging ligand has been achieved with the objective of constructing chain structures.[13] These can be regarded as multicomponent molecular systems and represent an important evolution in the development of molecular and supramolecular systems for catalysis, light to chemical energy conversion, and molecular-based devices.

Starting from this point, we wish to demonstrate that dithioxamides, and likewise dpcat, can be advantageously used to construct polymetallic systems by the "complexes as ligands" procedure. Within the scope in this paper we report the synthesis of binuclear complexes obtained using the chloro-bridge dimer $[Pd(\eta^3\text{-allyl})(\mu\text{-Cl})]_2$ as a substrate for the platinum dithioxamidate complexes. Several considerations led us to choose this organometallic substrate: first, the chemistry of Pd^{II} allyl complexes remains a widely studied theme which finds many important applications in the field of metal-promoted organic synthesis;[14] second, Pregosin's fertile idea of NOE "reporter ligands" could be applied to molecular systems such as **II** in order to determine solution structure;[15] and finally, the metal coordination square planes in **II** when L_nM is Pd(allyl) are stereogenic. Hence, binucleating dithioxamides bearing optically pure chiral substituents form diastereomers suitable for the allyl isomerization study of chiral chelate complexes, which is per se an interesting item.

Scheme 1



1, 4, 7: R = ethyl; **2, 5, 8**: R = benzyl; **3, 6, 9**: R = {S}-phenylethyl

Results and Discussion

The synthetic way to bimetallic Pt−Pd complexes starts from secondary dithioxamides as dithionic ligands, which easily react with *cis*-$[Pt(DMSO)PNCl_2]$ to give monochelate κ-S,S Pt ion pairs. These ion pairs can be dehydrohalogenated and in the form of rubeanate complexes quantitatively split the chloro-bridge dimer $[(\eta^3\text{-allyl})Pd(\mu\text{-Cl})]_2$ by means of the uncoordinated nitrogens (Scheme 1).

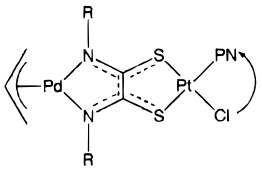
This synthetic procedure was previously followed by us to obtain Pt−Ru bimetallic complexes[7] and seems of general applicability. In fact from our experiments the capability of κ-S,S-coordinated dithioxamidate anions to chelate ML_n fragments after splitting $[L_nM(\mu\text{-Cl})]_2$ chloro-bridge dimers appears of widespread use. This observation should be emphasized per se, since the above synthetic procedure opens the way to a wide class of heterobimetallic complexes in which a rigid heteroatomic planar spacer ensures the transmission of electronic effects between two metal centers rigidly connected through the N,N and S,S donor sites of dithioxamidate anions.

(8) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26.
(9) Girgis, A. Y.; Sohn, Y. S.; Balch, A. L. *Inorg. Chem.* **1975**, *14*, 2327.
(10) Fox, G. A.; Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1991**, *30*, 2895.
(11) Hill, P. L.; Lee, L. J.; Younkin, T. R.; Orth, S. D.; McElwee-White, E. *Inorg. Chem.* **1997**, *36*, 5655.
(12) Paw, W.; Eisemberg, R. *Inorg. Chem.* **1997**, *36*, 2287.
(13) Bryngelson, P. A.; Haddad, T. S.; Doherty, N. M. *Absract of Papers*, 21th National Meeting of the American Chemical Society, New Orleans, LA, Spring 1996; American Chemical Society: Washington, DC, 1996; INOR 38.
(14) Hayashi, T. In *Catalytic Asymmetric Synthesis;* Ojima, I., Ed.; VCH: 1993; p 325. Trost, B. M. *Angew. Chem.* **1995**, *107*, 285.
(15) Albinati, A.; Kunz, R. W.; Amman, C. J.; Pregosin, P. S. *Organometallics* **1991**, *10*, 1800.

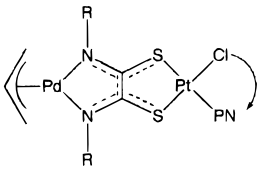
In addition, when $[L_nM(\mu\text{-Cl})]_2$ chloro-bridge dimers are prochiral substrates, their splitting by means of metal ligand complexes [LL′M′(H-DTO-κ-S,S′)] leads to binuclear species $[L_nM(\mu\text{-DTO})M'LL']$, where both metals are stereogenic. We have demonstrated that in these bimetallic complexes, when $L_nM = [Ru(p\text{-cymene})Cl]^+$ and $LL'M' = [(PN)ClPt]^+$, the stereogenicity of both platinum and ruthenium is fused in a bimetallic chiral axis.[7] When $L_nM = [Pd(allyl)]^+$ and $LL'M' = [(PN)\text{-}ClPt]^+$, the stereochemistry of the resulting binuclear complexes is slightly different, as it is described in the next paragraph.

Stereochemistry and Stereochemical Notation. The bimetallic dialkyldithioxbisamidate complexes **7**, **8**, and **9** are chiral: **7** and **8** were synthesized as racemic mixture of enantiomers, **9** as a 1:1 mixture of diastereomers owing to homochiral optically pure substituents on amidic nitrogens. The molecular asymmetry arises from the position of the η^3-coordinated allyl moiety, which is obliquely placed with respect to the metal square planes, and from the different monodentate substituents on platinum atom (PN and Cl). In this asymmetric geometrical array, both palladium and platinum are stereogenic. Although the species **7** and **8** contain two stereogenic centers, no more than two enantiomers can be envisaged for each of them. Any platinum substituent exchange affects the palladium configuration and vice versa, causing interconvertion of mutual enantiomers. This happens because the chirality of the molecule can be seen to spread over the whole coordination plane, which can be regarded as a plane of chirality.

To designate the configuration at platinum in the above planar chiral complexes, the stereonotation system developed for use in the Chemical Abstract Service registry system and in the Chemical Abstract Index[16] cannot be used. In fact, the stereochemical descriptor *SP-4*, which is the symmetry site term for square planar, four-coordinate geometry, cannot be followed by an additional digit since sulfur atoms on opposite side with respect to monodentate ligands PN and Cl have the same *CIP* priority. We suggest indicating the enantiomers of the bimetallic Pt−Pd(allyl) complexes by means of the direction C (clockwise) or A (anticlockwise) of the decreasing *CIP* priority sequence of the monodentate ligands on platinum when the molecule is viewed from the CH cusp of the allyl moiety:



A



C

The method adopted here is in agreement with the IUPAC recommendation of using the symbols C or A to designate chirality in systems other than tetrahedral (T-4) or octahedral (OC-6).[17]

(16) Brown, M. F.; Cook, B. R.; Sloan, T. E. *Inorg. Chem.* **1978**, *7*, 1563. Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1.

(17) *Nomenclature in Inorganic Chemistry, Recommendations;* Blackwell: Oxford, U.K., 1990; Chapter 10.

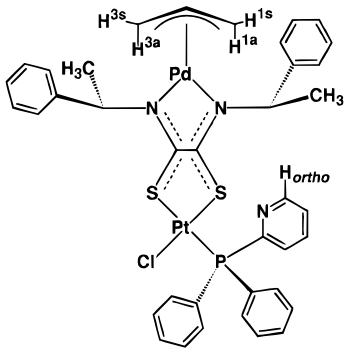


Figure 1. Schematic draw of **9** with labeled hydrogens.

Table 1. Selected NOE Percentage for 9

irradiated nucleous	selected NOE	percentage (%)
H^{1s} **9A**	H^{1a} **9A**	15
	CH_3 **9A** cis to P	1
	H^{3a} **9B**	15
H^{3s} **9B**	CH_3 **9B** trans to P	1
	CH_3 **9B** cis to P	∼0
	H^{3a} **9A**	15
H^{3s} **9A** + H^{1s} **9B**	H^{1a} **9B**	15
	CH_3 **9B** cis to P	1
	CH_3 **9A** trans to P	1
	H^{1s} **9A**	15
H^{1a} **9A** + H^{3a} **9B**	H^{3s} **9B**	15
	CH_3 (all resonances)	∼0
H_{ortho} (pyridine) **9A** + **9B**	CH_3 **9A** cis to P	1
	CH_3 **9B** cis to P	1

Thus complexes **7** and **8** can be termed as (A,C)-[(η^3-allyl)palladium(II)(μ-*N*,*N*′-(dialkyldithioxbisamidato-κ-*N*,*N*′-Pd-κ-*S*,*S*′-Pt)(2-(diphenylphospino)pyridine)(chloro)-platinum(II)], and diastereomers **9** as (A)- and (C)-[(η^3-allyl)palladium(II)(μ-(*N*,*N*′-{*S*}-diphenylethyldithioxbisamidato-κ-*N*,*N*′-Pd-κ-*S*,*S*′-Pt)(2-(diphenylphospino)pyridine)(chloro)platinum(II)], respectively.

Solution Structure of 9. In the absence of structural data, spatial connectivity between ligands and three-dimensional features of **9** could be investigated by NMR spectroscopy exploiting mono- and bidimensional NOE experiments. For this purpose it was necessary to unambiguously assign the proton resonances with conventional ^1H and ^{13}C 2-D homo- and heteronuclear correlation techniques. On the basis of NMR considerations it is impossible to say which diastereoisomer is which, although, when resolved, the resonances of each diastereoisomer (arbitrarily labeled respectively as **9A** and **9B**) can be separately grouped.

The resonance frequencies of corresponding protons in the two isomers are very close except for the allyl groups whose chemical shifts are much more sensitive to the relative orientation of the strictly close homochiral substituents than to the geometrical disposition of the peripheral phosphine. As a consequence, the H^{3s} and H^{3a} (trans to P) resonances of diastereoisomer **9A** overlap, respectively, H^{1s} and H^{1a} (cis to P) resonances of **9B**, while, though both resolved, the resonances H^{1s} and H^{1a} (cis to P) of **9A** are very close respectively to the H^{3s} and H^{3a} (trans to P) resonances of **9B** (Figure 1).

Selected NOEs for the diastereomeric mixture are reported in Table 1.

Eventhough selective irradiation of **9A** with respect to **9B** resonances could never be totally achieved, the results allowed us to draw some important conclusions.

First of all we can discriminate between methyl resonances cis or trans to P of each diastereoisomer. Second we can exploit the NOE between the methyls and the syn-allyl proton resonances to discriminate between allyl protons cis or trans to P of **9A** and **9B**.

Moreover it may be of interest that the NOE is observed between DTO methyls and syn- but not anti-allyl protons. Analogous selective NOEs for allyl derivatives have been previously reported by Pregosin et al. and have been attributed to CH syn twist toward the metal out of the allyl plane.[15,18] This distortion is rather general in allyl complexes and has been observed in the solid state both with X-rays[19,20] and neutrons[21] and has also been theoretically rationalized.[22]

Solution Dynamics of Complexes 7−9. Temperature produces important changes in ^{1}H NMR spectra of binuclear complexes. In fact the aliphatic DTO resonances of **7** and **8**, which appear at 298 K as a double ABC_3 in **7** and a double AB spin system in **8**, above the coalescence temperature, collapse, respectively, into two A_2B_3 and two A_2 spin systems. At the same time, the allyl proton resonances of **7** and **8**, which, in accordance with the chemical unequivalence of the opposite terminal atoms, show at room temperature resonances of an ABCDE spin system, collapse in both complexes into an A_2B_2C spin system. The high-temperature spectra are thus consistent with a dynamic process which makes the coordination plane of the metal a time-averaged symmetry plane, thus rendering the geminal $N-CH_2$ protons magnetically equivalent. The process also averages the resonances of the terminal allyl protons, but *not* those of DTO substituents (cis and trans to P, respectively).

Complex **9** shows at 298 K resonances of two diastereoisomers, **9A** and **9B**, in 1:1 molar ratio. Accordingly for each diastereoisomer two AB_3 spin system for the DTO aliphatic and two ABCDE spin systems for the allyl protons are observed. The high-temperature spectrum of **9** shows the collapse of the four AB_3 DTO aliphatic resonances into two AB_3 spin systems, while the two ABCDE allyl protons collapse into two A_2B_2C spin system with the C resonances overlapped (1,1′,2,2′-tetracloroethane was necessary to monitor coalescence and the high-temperature spectrum of **9**; at room temperature spectral features and isomerization rate of **9** in the two solvents are very similar).

The 2-D NOESY (EXSY) spectrum of **9** at 298 K sheds light on the intimate nature of the dynamic process. Figure 2 reports this spectrum together with a schematic representation of the proton exchanges suggested by its positive cross-peaks. Selective exchanges between different but not within the same diastereoisomer are observed.

Some of the possible π-allyl complexes' isomerization pathways can be ruled out on the basis of our findings: (i) $\eta^3-\eta^1$ isomerization, by the lack of syn−anti exchange; (ii) dissociation of the phosphine ligand, by the lack of DTO proton exchange from cis to trans to P and vice versa (phosphine dissociation has also been excluded on the basis of the absence of polarization transfer from ^{195}Pt satellites into the central peaks of the ^{31}P NMR spectrum); (iii) dissociation of [(PN)ClPt-(H-DTO)] by the lack of polarization transfer from the free metal ligand complex [(PN)ClPt(H-DTO)] to the binuclear complexes **9**. On the basis of conventional wisdom, rotation of the π-allyl moiety can also be excluded, believed "impossible" for palladium.[23]

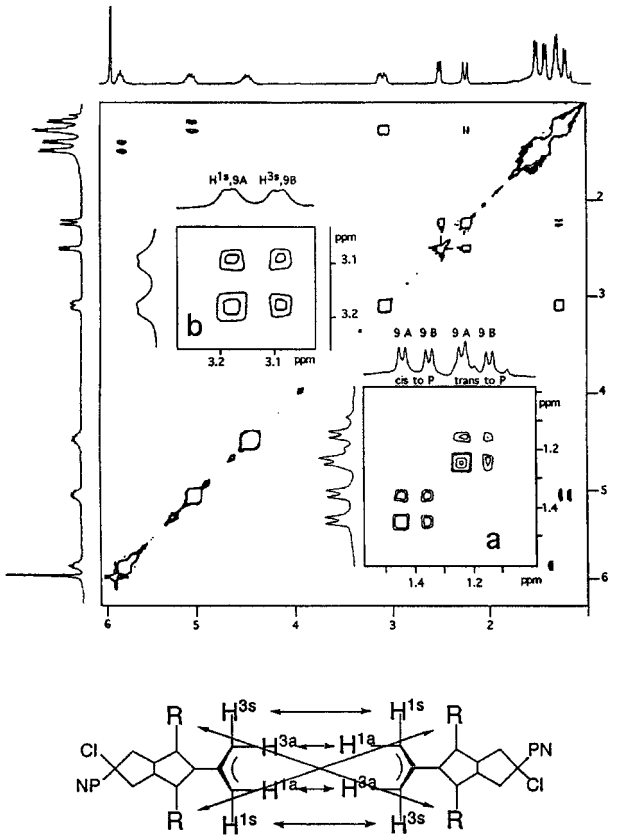


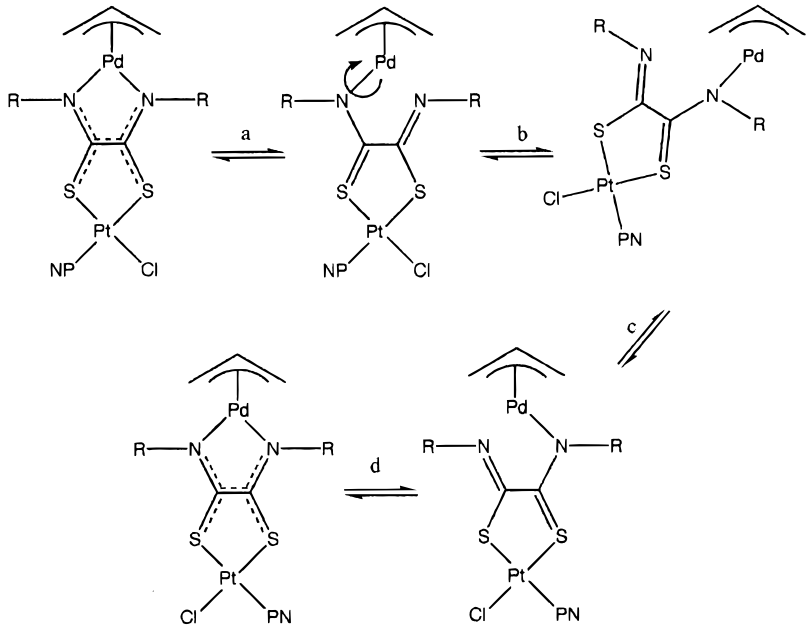
Figure 2. 2-D NOESY (EXSY) spectrum of **9** in 1,1′,2,2′-tetrachloroethane at 298 K. The negative cross-peaks shown in the whole spectrum are due to negative NOE. Positive cross-peaks, very close to the diagonal, are evidenced by the expansions: (a) DTO methyls exchange; (b) H^{3s} **9A** (trans to P)/H^{1s} **9B** (cis to P) exchange.

In conclusion, if we assume that the allyl does not rotate and that the phosphine and [(PN)ClPt(H-DTO)] do not dissociate, all our observations may be accommodated with a mechanism that 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 (steps b and c may be inverted). See Scheme 2.

According to this mechanism, the isomerization exchanges the position of the 1−3 allyl protons (from cis to P in one diastereoisomer to trans to P in the other and vice versa), but, of course, does not exchange the position of DTO protons, which, upon isomerization, retain their configuration with respect to P. This hypothesis is supported by the fact that Pd−N bond

(18) Albinati, A.; Amman, C.; Pregosin, P. S.; Ruegger, H. *Organometallics* **1990**, *9*, 1826−33.
(19) Gozum, J. E.; Pollina, D. M.; Jensen, J. A.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 2688.
(20) Faller, J. W.; Blankenship, C.; Whitmore, B. *Inorg. Chem.* **1985**, *24*, 4483.
(21) Goddard, R.; Kruger, C.; Mark, F.; Stansfield, R.; Zhang, X. *Organometallics* **1985**, *4*, 285.
(22) Klark, T.; Rhode, C.; Schleier, P. R. *Organometallics* **1983**, *2*, 1344.
(23) Vrieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975.

Scheme 2



R = ethyl, **7**; R = benzyl, **8**; R = {S}-phenylethyl, **9.**

Table 2. Activation Free Energy for the Racemization Process, $\Delta G^{\ddagger}$, and Charton *v* Parameters (See Text) for 7−9[a]

complex	$\Delta G^{\ddagger}$ (kJ·mol^{-1})	*v*
7, R = ethyl	62.2	0.56
8, R = benzyl	71.0	0.70
9, R = phenylethyl	83.5	0.99

[a] The linear regression analysis is $\Delta G^{\ddagger} = 46v + 38$, $R^2 = 0.993$; $P < 0.05$.

breaking has been already invoked as an isomerization source for other palladium allyl substrates.[15,24]

A possible alternative isomerization pathway which involves five-coordinate complexes seemed to us unlikely in a poorly coordinating solvent like chloroform and in the absence of coordinating species. We have also proved that added water does not significantly alter the isomerization rate. However the most convincing 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)$_2$HN$_2$C$_2$S$_2$-κ-*S*,*S*-Pd]. Presumably in the latter case the palladium sulfur bonds, differently from the weaker Pd−N bonds of our binuclear complexes, do not break precluding the dissociative mechanism. The contemporary absence of syn−anti proton exchange for the latter complex further supports that a high activation energy hinders allyl movements in these substrates.

$\Delta G^{\ddagger}$ values for both racemization and epimerization processes have been measured and are reported in Table 2. As one can see, allyl pseudorotation is relatively fast in **7** (R = ethyl) and becomes increasingly slower in **8** (R = benzyl) and in **9** (R = phenylethyl). These results indicate that the process is influenced by the nature of alkyl substituents on amidic nitrogens: the bulkier and more electron-withdrawing the substituents, the slower the isomerization rates. This suggests that rather than the Pd−N bond rupture, the rate-determining step of the process is the rotation around the residual Pd−N bond subsequent to the Pd−N bond rupture (fast reverse ring closure could minimize the kinetic effects of Pd−N bond rupture if DTO rotation and T-shaped intermediate isomerization were relatively slow). Accordingly $\Delta G^{\ddagger}$ significantly correlates with Charton's *v* values, parameters that correctly describe the internal rotation barrier in racemization of substituted biphenyl substrates.[26]

Table 3. Crystallographic Data for Complex 8

formula	$C_{36}H_{37}ClN_3O_2S_2PPdPt\cdot(CHCl_3)$
fw	1091.05
cryst form	orange, irregular
cryst dimens, mm	0.18 × 0.10 × 0.06
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	11.648(3)
b, Å	13.542(4)
c, Å	15.046(4)
α, deg	111.44(2)
β, deg	108.48(2)
γ, deg	91.43(2)
V, Å^3	2068(1)
Z	2
F(000)	1064
ρ_{calcd}, g/cm^3	1.752
μ, mm^{-1}	4.247
λ (graphite monochromated), Å	0.71073 (Mo Kα)
T, °C	25
2θ range, deg	3−51
no. of data colld (2θ−ω)	8211
no. of data refined (all)	7752
no. of data with $I \geq 2\sigma(I)$ (obs)	3987
no. of restraints/params	176/515
R^a(obs/all)	0.051/0.102
$wR2^b$(obs/all)	0.113/0.133
GOF[c]	0.791
largest diff peak and hole, e·Å^{-3}	1.609 and −1.302

[a] $R = [\sum||F_o| - |F_c||]/\sum|F_o|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] GOF $= [\sum w(F_o^2 - F_c^2)^2/(N_{observns} - N_{par})]^{1/2}$.

Crystal Structure of 8. The crystallographic cell contains two molecules simulating a center of symmetry

(24) Gogol, A.; Ornebro, J.; Grennberg, H.; Backball, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 3631.

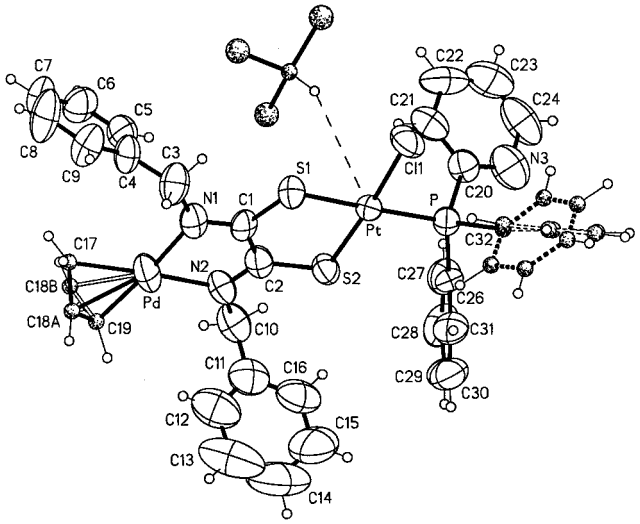


Figure 3. View of the asymmetric unit with atom-numbering scheme and thermal ellipsoids at 40% probability, while H size is arbitrary. The split conformations are represented by dashed-bond/shaded-ball, while the Pt···H interaction is represented by a shaded line. [Pt−S(1) = 2.312(3); Pt−S(2) = 2.258(3); Pt−P = 2.262(3); Pt−Cl(1) = 2.333(3); Pd−C(19) = 2.070(17); Pd−C(18B) = 2.09(4); Pd−C(18A) = 2.15(2); Pd−C(17) = 2.139(13); Pd−N(2) = 2.095(9); Pd−N(1) = 2.096(9); C(1)−C(2) = 1.506(15) Å and S(1)−C(1)−C(2)−S(2) = −1.1(12); S(2)−Pt−P = 92.95(11); S(2)−Pt−S(1) = 89.44(10); P−Pt−Cl(1) = 90.98(11); S(1)−Pt−Cl(1) = 86.65(11); C(19)−Pd−N(2) = 106.0(6); N(2)−Pd−N(1) = 78.7(4); N(1)−Pd−C(17) = 106.5(6)°].

evidenced by the diffraction data statistics and confirmed by the difficult model refinement. Due to the pseudo-symmetry effects, the crystal packing is better described in the centrosymmetric space group $P\bar{1}$ by using a unique independent disordered molecular unit. The ligand asymmetries appear as a molecular conformational disorder which causes the large thermal parameters of the benzyl substituents and the splitting of one ring orientation in the 2-(diphenylphosphino)-pyridine ligand. The complex flattening is determined by the planar DTO bridge chelating the "hard" palladium(II) via N atoms and the "soft" platinum(II) via the S atoms on the mean plane in whose respect the benzyl fragments are on opposite sides (Figure 3). By considering the allyl as a "short bite" chelating ligand, the Pd^{II} coordination might be considered a distorted square-planar geometry with the allyl central C(18) atom split symmetrically with respect to the coordination plane (50% of occupancy), as usually observed in analogous complexes.[27] The Pt^{II} atom adopts a regular square-planar geometry similar to that we have already reported for the analogous Pt−Ru complex.[7] However the crystal packing reveals an axial hydrogen interaction of the platinum with the cocrystallized chloroform molecule in the same asymmetric unit (Pt···H(38) = 3.275(1) Å, Pt···C(38) = 4.09(1) Å, Pt···H(38)−C(38) = 142(1)°). The H−Pt distance is significantly longer than the value we have reported in an analogous platinum−chloroform interaction;[28] this is probably due to the hindrance of the 2-(diphenylphosphino)pyridine ligand, which points the pyridine ring toward $CHCl_3$.

Experimental Section

General Considerations. Secondary dithioxamides were synthesized according to Hurd.[29] *cis*-$[Pt(Me_2SO)_2Cl_2]$[30] and *cis*-$[(PN)(Me_2SO)PtCl_2]$[31] were prepared following reported procedures. Other chemicals were commercially available and used as purchased.

^1H, ^{13}C, and ^{31}P NMR spectra were obtained on a Bruker ARX-300; external standards were $SiMe_4$ for ^{13}C and ^1H and 85% H_3PO_4 for ^{31}P. Coupling constants are reported in hertz, and chemical shifts in ppm assuming positive shifts downfield in all cases.

Free activation energies, $\Delta G^{\ddagger}$, were calculated in kJ mol^{-1} from the equation $\Delta G^{\ddagger} = 8.31T[23.76 + \ln(T/2\pi\Delta\nu)]$; T = coalescence temperature; $\Delta\nu$ = frequency difference (Hz) of coalesced resonances taken from the temperature frozen spectrum.

General Procedure for the Preparation of Ion Pair Dithioxamide Complexes {(PN)ClPt($H_2R_2N_2S_2C_2$)$^+$, (Cl^-)} (R = Ethyl, 1; R = Benzyl, 2; R = {*S*}-Phenylethyl, 3). A 1 mmol sample of *cis*-$[Pt(Me_2SO)(PN)Cl_2]$ (prepared in situ by mixing 1 mmol of *cis*-$[Pt(Me_2SO)_2Cl_2]$ and 1 mmol of PN) in the minimum amount of chloroform (∼10 mL) was reacted with a stoichiometric amount of $H_2R_2N_2C_2S_2$. The solution turned red and was allowed to stand at room temperature for 0.5 h. After this time to the concentrated solution petroleum ether 40−60 was added (∼50 mL). From the solution the {((PN)ClPt($H_2R_2N_2C_2S_2$))$^+$, (Cl^-)} ion pair immediately precipitated as magenta powders, which were separated from the uncolored supernatant and air-dried. Yields were higher than 90%.

{((PN)ClPt($H_2(C_2H_5)_2N_2S_2C_2$))$^+$, (Cl^-)} (1). ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): 13.14 (br s, 2H, N*H*); 8.82 (m, 1H, pyr*H-6*); 8.11 (m, 1H, pyr*H-3*); 7.78−7.28 (m, 12H, Ar*H* and pyr*H*); 3.83 (q, $^3J_{H-H}$ = 7.3, 2H, NCH_2); 3.34 (q,$^3J_{H-H}$= 7.3, 2H, NCH_2); 1.50 (t, $^3J_{H-H}$ = 7.3, 3H, CH_3); 1.33 (t, $^3J_{H-H}$ = 7.3, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 298 K): 150−124 (17C, Ar*C* and pyr*C*); 44.5 (1C, NCH_2); 44.1 (1C, NCH_2); 11.7 (1C, CH_3); 11.4 (1C, CH_3). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 298 K): 13.2($^1J_{Pt-P}$ = 3320, Pt−*P*). Anal (%) Calcd for $C_{23}H_{26}N_3PS_2Cl_2Pt$: C, 39.15; H, 3.71; N, 5.96; S, 9.09; Cl, 10.05. Found: C, 38.98; H, 3.68; N, 6.03; S, 9.32; Cl 9.87.

{(PN)ClPt($H_2(C_7H_7)_2N_2S_2C_2$)$^+$, (Cl^-)} (2). ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): 13.69 (br s, 2H, N*H*); 8.79 (m, 1H, pyr*H-6*); 8.11 (m, 1H, pyr*H-3*); 7.84−7.08 (m, 22H, Ar*H* and pyr*H*); 4.94 (s, 2H, NCH_2); 4.48 (s, 2H, NCH_2). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 298 K): 150.5−125.0 (29C, Ar*C* and pyr*C*); 51.9 (1C, NCH_2), 51.6 (1C, NCH_2). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 298 K): 13.1 ($^1J_{Pt-P}$ = 3313, Pt-*P*). Anal (%) Calcd for $C_{33}H_{30}N_3PS_2Cl_2Pt$: C, 47.77; H, 3.64; N, 5.06; S, 7.73; Cl, 8.55. Found: C, 48.10; H, 3.56; N, 4.98; S, 7.41; Cl, 8.61.

{(PN)ClPt(H_2({*S*}-$CHCH_3Ph)_2N_2S_2C_2$)$^+$, (Cl^-)} (3). ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): 13.89 (br s, 2H, N*H*); 8.77 (m, 1H, pyr*H-6*); 8.11 (m, 1H, pyr*H-3*); 7.79−7.06 (m, 22H, Ar*H* and pyr*H*); 5.34 (q,^3J = 6.6, 1H, NC*H*Ph); 5.22 (q,$^3J_{H-H}$ = 6.6, 1H, NC*H*Ph); 1.91 (d,$^3J_{H-H}$ = 6.6, 3H, CH_3); 1.79 (d, $^3J_{H-H}$ = 6.6, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 298 K):

(25) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *99*, 2079. Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

(26) Charton, M.; Charton, B. *J. Am. Chem. Soc.* **1975**, *97*, 6472. Roussel, C.; Lidén, A.; Chanon M.; Metzger, J.; Sandström, J. *J. Am. Chem. Soc.* **1976**, *98*, 2847, and references therein. Charton, M. *J. Org. Chem.* **1977**, *42*, 2528.

(27) Schaffner, S.; Macko, L.; Neuburger, M. Zehnder, M. *Helv. Chim. Acta* **1997**, *80*, 463.

(28) Lanza, S.; Bruno, G.; Nicolò, F. *Acta Crystallogr., Sect. C* **1990**, *46*, 765.

(29) Hurd, R. N.; De La Mater J.; McEleheny, G. C.; Tuner, R. J.; Wallingford, V. H. *J. Org. Chem.* **1961**, *26*, 3980.

(30) Kukushkin, Y. N.; Viaz'mesnkii Y. E.; Zorina, L. I. *Russ. J. Inorg. Chem.* **1968**, 835.

(31) Arena, C. G.; Ciani, G.; Drommi, D.; Faraone, F.; Proserpio, D. M.; Rotondo, E. *J. Organomet. Chem.* **1994**, *71*, 848.

151.0−124.0 (29C, Ar*C* and pyr*C*); 60.3 (2C, N*C*HPh); 21.8 (1C, *C*H_3); 21.6 (1C, *C*H_3). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 298 K): 13.5 ($^1J_{Pt-P}$ = 3307, Pt−*P*). Anal (%) Calcd for $C_{35}H_{34}N_3PS_2Cl_2Pt$: C, 49.01; H, 4.00; N, 4.90; S, 7.48; Cl, 8.27. Found: C, 49.13; H, 4.10; N, 5.12; S, 7.32; Cl, 8.05.

General Procedure for the Preparation of Dithioxamidato Complexes [(PN)ClPt($HR_2N_2S_2C_2$)] (R = Ethyl, 4; R = Benzyl, 5; R = {*S*}-Phenylethyl, 6). A 200 mg sample of sodium bicarbonate was added to 1 mmol of the above ion pairs dissolved in the minimum amount of chloroform (∼20 mL). The magenta solution immediately turned to orange; after 0.5 h of stirring, the sodium bicarbonate was removed by filtration and the orange solution was concentrated to a small volume (∼1 mL). [(PN)ClPt($HR_2N_2C_2S_2$)] complexes **4**−**6** precipitated as orange powders, which were collected and air-dried. Yields were higher than 90%.

[(PN)ClPt($H(C_2H_5)_2N_2S_2C_2$)] (4). ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): 8.74 (m, 1H, pyr *H-6*) 8.39 (m, 1H, pyr*H-3*); 7.87−7.27 (m, 12H, ArH and pyr*H*); 3.71 (q, $^3J_{H-H}$ = 7.3, 2H, N*CH*$_2$) 3.28 (q, $^3J_{H-H}$ = 7.3, 2H, N*CH*$_2$); 1.34 (t, $^3J_{H-H}$ = 7.3, 3H, *CH*$_3$); 1.17 (t, $^3J_{H-H}$ = 7.3, 3H, *CH*$_3$). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 298 K): 186.8 (d, $^3J_{C-P}$ = 3, 1C); 172.9 (d, $^3J_{C-P}$ = 11, 1C, *CS* trans to P); 150.5−124.9 (17C, Ar*C* and pyr*C*); 45.3 (1C, N*CH*$_2$); 41.8 (1C, N*CH*$_2$); 14.5 (1C, *CH*$_3$); 13.1 (1C, *CH*$_3$). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 298 K): 16.6 ($^1J_{Pt-P}$ = 3408, Pt−*P*). Anal(%) Calcd for $C_{23}H_{25}N_3PS_2ClPt$: C, 41.29; H, 3.77; N, 6.28; S, 9.58; Cl, 5.30. Found: C, 41.15; H, 3.67; N, 6.11; S, 9.62; Cl, 5,47.

[(PN)ClPt($H(C_7H_7)_2N_2S_2C_2$)] (5). ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): 8.76 (m, 1H, pyr*H-6*); 8.39 (m, 1H, pyr*H-3*); 7.86−7.08 (m, 22H, Ar*H* and pyr*H)*; 4.84 (s, 2H, N*CH*$_2$); 4.40 (s, 2H, N*CH*$_2$). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 298 K): 188.0 (d, $^3J_{C-P}$ = 3, 1C, *CS* cis to P); 185.4 (d, $^3J_{C-P}$ = 8, 1C, *CS* trans to P); 150.1−124.5 (29 C, Ar*C* and pyr*C*); 54.5 (1C, N*CH*$_2$); 51.0 (1C, N*CH*$_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 298 K): 16.2 ($^1J_{Pt-P}$ = 3400, Pt−*P*). Anal (%) Calcd for $C_{33}H_{29}N_3PS_2ClPt$: C, 49.97; H, 3.68; N, 5.30; S, 8.08; Cl, 4.47. Found: C, 50.15; H, 3.76; N, 5.08; S, 8.23; Cl, 4.58.

[(PN)ClPt(H({*S*}-$CHCH_3Ph)_2N_2S_2C_2$)] (6). ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): 8.74 (m, 1H, pyr*H-6*); 8.43 (m, 1H, pyr*H-3*); 7.88−7.10(m, 22H, Ar*H* and pyr*H*); 5.42 (q, $^3J_{H-H}$ = 6.6, 1H, N*CH*Ph); 4.74 (q, $^3J_{H-H}$ = 6.6, 1H, N*CH*Ph); 1.64 (d, $^3J_{H-H}$ = 6.6, 3H, *CH*$_3$); 1.40 (d, $^3J_{H-H}$ = 6.6, 3H, *CH*$_3$). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 298 K): 186.5 (d, $^3J_{C-P}$ = 3, 1C, *CS* cis to P); 177,8 (d, $^3J_{C-P}$ = 9, 1C, *CS* trans to P); 149.0−124.3 (29C, Ar*C* and pyr*C*); 58.8 (1C, N*CH*Ph); 56.4 (1C, N*CH*Ph); 22.2 (1C, *CH*$_3$); 20.9 (1C, *CH*$_3$). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 298 K): 13.5 ($^1J_{Pt-P}$ = 3307, Pt−*P*). Anal (%) Calcd for $C_{35}H_{33}N_3PS_2ClPt$: C, 52.12; H, 4.17; N, 5.11; S, 7.80; Cl, 4.31. Found: C, 51.93; H, 4.20; N, 5.14; S, 7.66; Cl, 4.05.

General Procedure for the Preparation of Binuclear Dithioxbisamidato Complexes [(PN)ClPt(μ-$R_2N_2S_2C_2$-κ-*S*,*S*-Pt-κ-*N*,-Pd)Pd(η^3-C_3H_5)] (η^3-C_3H_5 = η^3-Allyl; R = Ethyl, 7; R = Benzyl, 8; R = {*S*}-Phenylethyl, 9). A 1 mmol sample of [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ was dissolved in about 30 mL of a 70:30 v/v chloroform/methanol mixture and reacted with a half molar quantity of [(PN)ClPt($HR_2N_2S_2C_2$)] complexes. The solution, which turned deep red, was allowed to stand for 2 h. The solvents were removed and the crude products, redissolved in the minimum amount of chloroform (about 10 mL), placed on an alumina column, and equilibrated with light petroleum. The desired products were collected as orange eluates and concentrated to a small volume (about 1 mL). By adding petroleum ether 40−60 (about 30 mL), bimetallic complexes precipitated as orange powders. Yields were higher than 80%.

[(PN)ClPt(μ-*N*,*N*′-$(C_2H_5)_2N_2S_2C_2$-κ-*S*,*S*′-Ptκ-*N*,*N*′-Pd)(η^3-allyl)Pd] (7). ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): 8.68 (m, 1H, pyr *H-6*); 8.47(m, 1H, pyr*H-3*); 7.80÷7.13, (12 H, Ar*H* and pyr*H*); 5.39 (m, 1H, allyl C*H*); 4.81 (dq, $^2J_{H-H}$ = 13.8, $^3J_{H-H}$ = 6.8, 2H, N*CH*$_2$ cis to P, part AB of ABC_3); 3.38 (dq, $^2J_{H-H}$ = 13.8, $^3J_{H-H}$ = 6.8, 2H, N*CH*$_2$ trans to P, part AB of ABC_3); 1.15 (t, $^3J_{H-H}$ = $^3J_{H-H}$ = 6.8, 3H, *CH*$_3$ trans to P, part C_3 of ABC_3); 0.95, (t, $^3J_{H-H}$ = $^3J_{H-H}$ = 6.8, 3H, *CH*$_3$ cis to P, part C_3 of ABC_3); 5.42 (m, 1H, central-allyl, C*H*); 3.52 (m, $^3J_{H-H}$ = 6.9, 1H, syn-allyl C*H*H); 3.50 (m, $^3J_{H-H}$ = 6.9, 1H, syn-allyl C*H*H); 2.91 (m,$^3J_{H-H}$ = 12.7, 1H, anti-allyl CH*H*); 2.89, (m, $^3J_{H-H}$= 12.7, 1H, anti-allyl CH*H*). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 298 K): 190.8 (d, $^3J_{C-P}$ = 11, 1C, *CS* trans to P); *CS* 190.3 (d, $^3J_{C-P}$ = 2, 1C, *CS* cis to P); 154.6 −124.3 (17C, Ar*C* and pyr*C*); 115.5 (1C, central-allyl *C*H); 58.0 (1C, allyl *C*H_2); 57.9 (1C, allyl *C*H_2); 52.8 (1C, N*CH*$_2$); 52.1 (1C, N*CH*$_2$); 13.0 (1C, *CH*$_3$); 12.7 (1C, *CH*$_3$). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 298 K): 17.3 ($^1J_{Pt-P}$ = 3267, Pt−*P*). Anal (%) Calcd for $C_{26}H_{29}N_3PS_2ClPdPt$: C, 38.33, H, 3.59; N, 5.16; S, 7.83; Cl, 4.30. Found: C, 38.61; H, 3.71; N, 5.25; S, 8.05; Cl, 4.52.

[(PN)ClPt(μ-*N*,*N*′-$(C_7H_7)_2N_2S_2C_2$κ-*S*,*S*′-Ptκ-*N*,*N*′−Pd)-(η^3−allyl)Pd] (8). ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): 8.76 (m, 1H, pyr*H*-6); 8.55 (m, 1H, pyr*H-3*); 7.60−7.00 (m, 22 H, Ar*H* and pyr*H*); 5.10 (AB q,^1J = 15, 2H, N*CH*$_2$ cis to P); 4.55 (AB q, ^1J = 15, 2H, N*CH*$_2$ trans to P); 4.90 (m, 1H, central-allyl C*H*); 3.10 (m, $^3J_{H-H}$ = 5.8, 1H, syn-allyl C*H* H trans to P); 2.86 (m, $^3J_{H-H}$ = 5.8, 1H, syn-allyl C*H* H cis to P); 2.29 (m, $^3J_{H-H}$ = 12, 1H, anti-allyl CH*H* cis to P); 2.24 (m,$^3J_{H-H}$ = 12, 1H, anti-allyl CH*H* trans to P). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 298 K): 192.2 (d, $^3J_{C-P}$ = 2, 1C, *CS* cis to P); 192.1 (d,$^3J_{C-P}$ = 10, 1C, *CS* trans to P); 150.1−123.0, 29C, Ar*C* and pyr*C*); 60.7 (1C, N*CH*$_2$ cis to P); 60.1 (1C, N*CH*$_2$ trans to P); 114.7 (1C, central-allyl *C*H); 59.1 (1C, allyl *C*H_2 cis to P); 58.8 1C, allyl *C*H_2 trans to P). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 298 K): 17.1 (Pt−*P*, $^1J_{Pt-P}$ = 3272). Anal (%) Calcd for $C_{36}H_{33}N_3PS_2ClPdPt$: C, 46.05; H, 3.55; N, 4.48; S, 6.82; Cl, 3.73. Found: C, 46.16; H, 3.61; N, 4.51; S, 6.70; Cl, 3.57.

[(PN)ClPt(μ-*N*,*N*′-({*S*}-diphenylethyl)dithioxamidatoκ-*S*,*S*′-Pt κ-*N*,*N*′-Pd) (η^3-allyl)Pd] (9). ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): 8.67 (m, 1 H, pyr*H-6*); 8.46 (m, 1H, pyr *H-3*); 7.00−7.70 (m, 22 H, Ar*H* and pyr*H* **9A and 9B**); 5.85 (q,$^3J_{H-H}$ = 6.6, 0.5H, N*CH*Ph cis to P **9A**); 5.81 (q,$^3J_{H-H}$ = 6.6, 0.5H, N*CH*Ph cis to P **9B**); 5.14 (q,$^3J_{H-H}$ = 6.6, 0.5H, N*CH*Ph trans to P **9A**); 5.10 (q, $^3J_{H-H}$ = 6.6, 0.5H, N*CH*Ph trans to P **9B**); 4.46 (m, 1H, central-allyl C*H* **9A and 9B**); 3.15 (m, $^3J_{H-H}$ = 6.7, 0.5H, syn-allyl C*H*H cis to P **9A**); 3.06 (m, $^3J_{H-H}$ = 6.7, 0.5H, syn-allyl C*H*H trans to P **9B**); 2.49 (m, $^3J_{H-H}$ = 6.6, 1H, syn-allyl CH*H* overlapped cis to P **9A** and trans to P **9B**); 2.24 (m, 1H, anti-allyl CH*H* overlapped trans to P **9B** and cis to P **9A**); 1.33 (m partially obscured by the methyls, 0.5H, anti-allyl CH*H* cis to P **9A**); 1.28 (m partially obscured by the methyls, 0.5H, anti-allyl CH*H* trans to P **9B**); 1.53 (d, ^3J = 6.6 (1.5H, *CH*$_3$ cis to P **9A**); 1.44 (d, ^3J = 6.6, 1.5H, *CH*$_3$ cis to P **9B**); 1.33 (d, $^3J_{H-H}$ = 6.6, 1.5H, *CH*$_3$ trans to P **9A**); 1.23 (d, $^3J_{H-H}$ = 6.6, 1.5H, *CH*$_3$ trans to P **9B**). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 298 K): 190.8 (d,$^3J_{C-P}$=10, 0.5C, *CS* trans to P **9A**); 190.4 (d, $^3J_{C-P}$ = 10, 0.5C, *CS* trans to P **9B**); 190.1 (d, $^3J_{C-P}$ = 3, 0.5C, *CS* cis to P **9A**); 189.8 (d, $^3J_{C-P}$=3, 0.5C, *CS* cis to P **9A**); 150.0−125.0 (29C, Ar*C* and pyr*C*); 60.5 (1C, N*CH*Ph cis to P overlapped **9A and 9B**); 59.9 (1C, N*CH*Ph trans to P overlapped **9A and 9B**); 111.9 (1C, central-allyl *C*H); 58.7 (1C, allyl *C*H2 cis to P overlapped **9A and 9B**); 57.9 (1C, allyl *C*H_2 trans to P overlapped **9A and 9B**); 18.5 (0.5C, *CH*$_3$ cis to P, **9A**); 17.4 (0.5C, *CH*$_3$ cis to P **9B**); 18.3 (0.5C, *CH*$_3$ trans to P **9A**); 17.2 (0.5C, *CH*$_3$ trans to P **9B**). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 298 K): 17.5 (0.5P, $^1J_{Pt-P}$ = 3273, Pt−*P*); 17.4 (0.5P, $^1J_{Pt-P}$ = 3273, Pt−*P*). Anal (%) Calcd for $C_{38}H_{37}N_3PS_2ClPdPt$: C, 46.20; H, 3.86; N, 4.35; S, 6.62; Cl, 3.62. Found: C, 46.42; H, 3.71; N, 4.21; S, 6.56; Cl, 3.41.

X-ray Crystallographic Studies of 8. Diffraction data of a suitable crystal were collected at room temperature on a Siemens P4 automatic four-circle diffractometer by using graphite-monochromated Mo Kα radiation. Lattice parameters were obtained from least-squares refinement of the setting angles of 35 reflections with 11° ≤ 2θ ≤ 30°. No sign of crystal deterioration was revealed during the data collection. The

reflection intensities, collected by variable speed $\omega-2\theta$ scan technique, were evaluated by a profile fitting among 2θ shell procedure[32] and then corrected for Lorentz−polarization effects. An absorption correction was applied by fitting a pseudo-ellipsoid to the azimutal scan data of 20 high χ reflections[33] (R_{int} $a/p = 12.7/3.9\%$, $T_{min/max} = 0.51/1.00$). Data reduction has been performed with the SHELXTL-PLUS system.[34]

The statistics $|E^2 - 1| = 0.807$ (expected 0.736 for non- and 0.968 for centrosymmetric packing) pointed to the acentric arrangement. However each attempt to complete/refine the crystal modeling in $P1$ was unsuccessful due to the very large correlation between the two molecules into the cell. Therefore the crystal structure was solved by the standard Patterson method and subsequently completed by a combination of least-squares technique and Fourier syntheses in the centrosymmetric space group $P\bar{1}$, treating the conformational disorder by suitable restraints. H atoms were included in the refinement in the "riding model" method with the X−H bond geometry and the H isotropic displacement parameter depending on the parent atom X. The refinement, with all non hydrogen atoms anisotropic and minimizing the function $\sum w(F_o^2 - F_c^2)^2$, was carried out with the full-matrix least-squares technique, based on all independent F^2, with SHELXL97.[35] The final weighting scheme was $w^{-1} = [\sigma^2(F_o)^2 + (0.0238(F_o^2 + 2F_c^2))^2]$. A parameter for extinction correction was included into the last refinement cycles and assumed the final value $1.9(2) \times 10^{-3}$. In the last difference Fourier map the significant density residuals were up to 1.56 e Å^{-3} at 1 Å from the Pt atom.

Final geometrical calculations and drawings were carried out with the PARST program[36] and the XPW utility of the Siemens package, respectively.

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

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(32) Diamond, R. *Acta Crystallogr., Sect. A* **1969**, *25*, 43.
(33) Kopfmann, G.; Huber, R. *Acta Crystallogr., Sect. A* **1968**, *24*, 348.
(34) Sheldrick, G. M. *SHELXTL-PLUS*, version 4.2; Siemens Analytical X-ray Instruments Inc., Madison, WI, 1991.
(35) Sheldrick, G. M. *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Germany, 1997.
(36) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95 (version locally modified).