Rhodium Complexes with the Chelating and Binucleating Ligands $P(CH_2CH_2Py)_nPh_{3-n}$ (Py = 2-Pyridyl; n = 1, 2): Structures and Fluxional Behavior

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Received June 2, 1999

Several rhodium(I) complexes of the type [RhX(CO)($PePy_2$)], [Rh(diene)($PePy$)]$^+$, and [Rh(diene)($PePy_2$)]$^+$ ($PePy_n$ = $P(CH_2CH_2Py)_nPh_{3-n}$; Py = 2-pyridyl; n = 1, 2) have been prepared. The two former are square planar; the latter are pentacoordinated for diene = tetrafluorobenzobarrelene or norbornadiene (confirmed by X-ray diffraction), but an equilibrium of 4- and 5-coordinate isomers exists in solution for diene = 1,5-cyclooctadiene. The fluxional behavior of all these complexes is studied by NMR spectroscopy. The complex [Rh(NBD)($PePy_2$)]PF_6·Cl_2CH_2 crystallizes in the monoclinic space group $P2_1/n$ with a = 8.455(1) Å, b = 18.068(3) Å, c = 19.729(3) Å, β = 99.658(3)°, and Z = 4. The complexes [Rh(diene)($PePy_2$)]$^+$ react with CO to give the dimeric complex $[Rh_2(CO)_2\{P(CH_2CH_2Py)_2Ph\}_2](BF_4)_2$ with the pyridylphosphine acting as P,N-chelating and P,N-bridging.

Introduction

There is interest in the chemistry of Rh(I) complexes with ligands containing pendant arms that can either coordinate or leave a vacant position, since this may facilitate a catalytic cycle. A common problem in the study of these complexes is that in square-planar complexes there is usually fast exchange of the pendant and coordinated arms of the multidentate ligand, a situation which is difficult to distinguish from pentacoordination. The problem has been extensively studied in substituted hydrotris(pyrazolyl)borate (Tp^R) complexes, for which many solid-state structures have been described, as well as the existence of equilibria between square-planar and pentacoordinated complexes, boat-to-boat conformational changes, and intramolecular substitution processes.[1] Recently, an extreme example has been reported: The compound Tp^{iPr}Rh(NBD) (NBD = norbornadiene) crystallizes in two coordination geometries in the same unit cell.[2] This case provides structural information which is lost when the complexes are studied by NMR spectroscopy in solution because of the fast exchange between both structures and between coordinated and uncoordinated arms in the square-planar isomer. The authors have characterized the complexes using IR spectroscopy for the assignment of the solution structures. For other multidentate ligands, the situation is less known, since less structural and dynamic information is available.

Related behavior is possible for 2-(phosphino)pyridines, which have been extensively used as homo- and heterometallic binucleating ligands. Some representative coordination modes are shown in Chart 1. Thus, 2-(diphenylphosphino)pyridine gives dimeric complexes of the type **A**, whereas 2,6-bis-(diphenylphosphino)pyridine allows the synthesis of linear compounds of higher nuclearity of the type **B**.[3] In these complexes, two binucleating ligands are coordinated to the metal center in mutually trans positions, with the remaining ligands also in trans positions. Budzelaar et al. have used a group of binucleating 2-pyridyldiphosphines capable of forming metal complexes in which the P and N atoms are in mutually cis positions, as in type **C**.[4]

2-Pyridylphosphines with the P atom separated from the Py group by one or two methylene links, capable of forming five- and six-membered rings by chelation, have been much less studied and seem to show little tendency to behave as bridging ligands.[3,5]

We report here the syntheses and structures of complexes of rhodium(I) with the ligands $PePy_n$ ($PePy_n$ = $P(CH_2CH_2Py)_nPh_{3-n}$; Py = 2-pyridyl; n = 1, 2). PePy can act as a bidentate ligand, whereas $PePy_2$ is capable of behaving either as a bidentate or as a tridentate chelating ligand, to give square-planar and pentacoordinated structures (**D** and **E**), and also as a bridging

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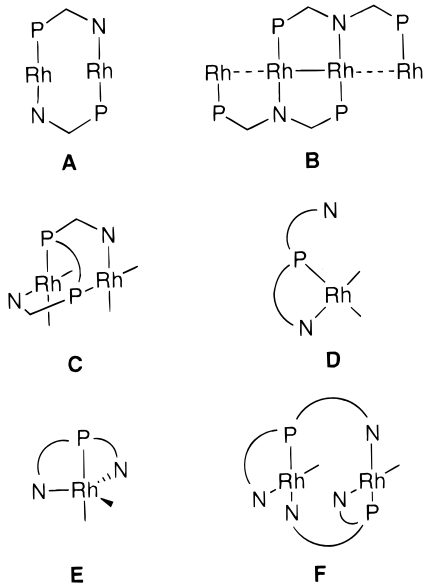
10.1021/ic990634a CCC: $19.00
Published on Web 01/27/2000

Chart 1



ligand, giving complexes of type **F**. The results obtained for PePy assist in the interpretation of the more complex behavior of $PePy_2$.

Results and Discussion

The compounds prepared, along with relevant spectroscopic data, are listed in Table 1. Their syntheses are straightforward. $[RhCl(CO)(PePy_2)]$ (**1**) was prepared by addition of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ to a solution containing a stoichiometric amount of $PePy_2$. Complex **1** reacted with an excess of NaI to give $[RhI(CO)(PePy_2)]$ (**2**) and with $AgBF_4$ or with $TlBF_4$ to give $[Rh_2(CO)_2(PePy_2)_2](BF_4)_2$ (**3**).

The diolefin complexes, $[Rh(TFB)(PePy)](PF_6)$ (**4**; TFB = tetrafluorobenzobarrelene), $[Rh(COD)(PePy)](BF_4)$ (**5**; COD = 1,5-cyclooctadiene), $([Rh(NBD)(PePy_2)](PF_6)$ (**6**; NBD = norbornadiene), $[Rh(TFB)(PePy_2)](PF_6)$ (**7**), and $[Rh(COD)(PePy_2)](BF_4)$ (**8**), were prepared as yellow crystalline solids by reaction of PePy or $PePy_2$ with the corresponding dimers $[Rh_2(\mu\text{-}Cl)_2(diene)_2]$ in the presence of $TlBF_4$, $TlPF_6$, or $AgBF_4$. Bubbling CO through solutions containing $[Rh(diene)(PePy_2)]^+$ is another way of obtaining complex **3** in high yield.

Halo Carbonyl Complexes (1 and 2). For ligands containing pyridyl groups, the analysis of the IR spectra indicates whether they are coordinated or not, by the changes in frequency of $\nu_{Py}(CN)$.[6,7] The uncoordinated Py groups exhibit this band at 1590 cm^{-1} (PePy) and 1592 cm^{-1} ($PePy_2$), whereas when they are coordinated, the band moves to 1600−1610 cm^{-1}. The IR spectra of **1** and **2** in the solid state show two such bands, one due to coordinated and one to free Py. No significant changes are observed in their IR spectra in CH_2Cl_2 solution (Table 1). Thus, only one of the two Py groups is coordinated and the compounds are square-planar. Since their IR spectra are almost identical to that of [RhCl(CO)(PePy)], characterized previously by Pignolet et al.,[6] **1** and **2** are assigned the same stereochemistry with the CO and the phosphine ligands in mutually cis positions.

In the ^1H NMR spectra, the chemical shift of H^6 of the Py groups is also very sensitive to coordination.[8,9] At room temperature, **1** and **2** exhibit fast exchange of their Py groups, which renders them equivalent (Scheme 1). For **1**, the low exchange limit is not reached because T_c is very low (the H^6 signals are still in coalescence at −82 °C), thus preventing the evaluation of $\Delta G^{\ddagger}$. Fortunately, the exchange is slower in **2**, with $T_c = -70$ °C for the H^6 signals ($k = 840\ s^{-1}$, $\Delta G^{\ddagger} = 37.7$ kJ mol^{-1}). The low-temperature spectrum (Table 1) indicates that only one Py group is coordinated, again supporting a square-planar structure with a pendant Py arm, in accordance with the IR spectroscopic data. The variation of rate of Py exchange with the halo ligand (Cl > I) is consistent with the expected associative mechanism, which should be faster the more electrophilic the Rh center, i.e., the more electronegative and less π-donating the halo ligand.

The six-membered ring formed by P,N coordination of the ligand is nonplanar, although the barrier to conformational change averaging it to planar is very low, as reported for related complexes with PePy.[6,9] Complexes **1** and **2** can give rise to two chiral diastereoisomers (**A** and **B** in Scheme 1), each with their corresponding enantiomers (**A′** and **B′**). Two movements are possible in these complexes, as shown in Scheme 1: (i) the Py exchange just discussed and (ii) an inversion of the conformation of the nonplanar metallacycle (boat inversion for short). It can be seen in Scheme 1 that, although racemization (**A** to **A′** or **B** to **B′**) needs the two movements, just any one of the two is enough to convert one diastereoisomer into the other with neglect of chirality (**A** to either **B** or **B′**; **B** to either or **A′**). Since NMR is not sensitive to optical activity, different diastereoisomers will be observed by NMR only if both movements are frozen. Conversely, the fact that only one product is observed for **2** below coalescence of the Py exchange indicates that the boat inversion is still fast at that temperature and is responsible for the interconversion of diastereoisomers.

It is worth noting that the opposite order of rate for these two movements is found in the complexes $[Rh(diene)\{P(bzN)_3\}](BF_4)$ (bzN = 2-((dimethylamino)methyl)phenyl), where the inversion of the boat is much slower than the exchange of amine groups, producing exchange with retention of configuration of the boat. Thus the nature of the chelate group exerts a dramatic influence on the ease of boat inversion, even though both ligands give rise to six-membered chelating rings including one ortho-substituted aromatic ring.[10] The low energy associated with the conformational change in PePy ligands is possibly associated with the presence of three consecutive sp^3 stereocenters, which makes possible not only boat conformations but also chairlike and twist conformations. The two extreme boat conformations may be connected by twisted conformations which are not much higher in energy.

$[Rh_2(CO)_2(PePy_2)_2](BF_4)_2$ (3). The solid-state IR spectrum of **3** shows two CO stretching bands at 1978 and 2002 cm^{-1} separated by only 24 cm^{-1}. This suggests a dimeric structure in which two CO ligands are located in different metallic centers

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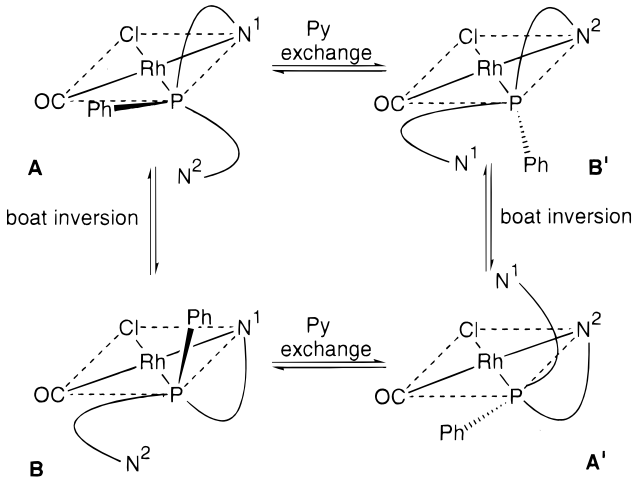
Table 1. Relevant Spectroscopic Data for Complexes **1**−**8**

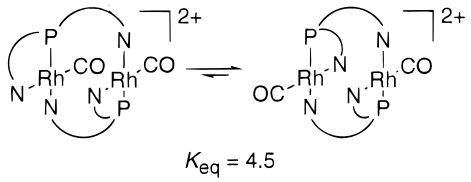
compound	*T*, °C	IR: $\nu(CN)_{Py}$, cm^{-1} solid	IR: $\nu(CN)_{Py}$, cm^{-1} Cl_2CH_2	1H NMR: δ(Py H^6), ppm[a]	^{1}H NMR: δ(olefinic signals), ppm[a]	^{31}P NMR: δ, ppm ($^1J_{RhP}$, Hz)
[RhCl(CO)($PePy_2$)] (**1**)[b]	rt	1606, 1587	1608, 1596	8.79 (2)		44.0 (161.5)
[RhI(CO)($PePy_2$)] (**2**)[c]	rt	1605, 1593	1608, 1595	8.90 (2)		41.8 (168.4)
	−90			9.12 (1), 8.49 (1)		
$[Rh_2(CO)_2(PePy_2)_2](BF_4)_2$ (**3**)[d,e]	rt	1606	1608	(a) 8.76 (1), 7.81 (1)		45.7 (148.5)
				(b) 8.66 (1), 7.72 (1)		47.3 (148.2)
[Rh(TFB)(PePy)](PF_6) (**4**)[d]	rt	1609	1602	8.67 (1)	5.70 (2), 3.65 (2)	34.0 (166.9)
[Rh(COD)(PePy)](BF_4) (**5**)[d]	rt	1606	1608	8.87 (1)	5.26 (2), 3.79 (2)	34.2 (148.9)
[Rh(NBD)($PePy_2$)](BF_4) (**6**)[b]	rt	1600	1608	8.87 (2)	3.43 (4)	35.5 (144.7)
	−90					
[Rh(TFB)($PePy_2$)](PF_6) (**7**)[b]	rt	1604	1608	8.94 (2)	3.45 (4)	43.4 (146.3)
	−90			10.07 (1), 7.73 (1)	5.38 (1), 4.95 (1), 1.90 (1), 1.25 (1)	47.9 (145.8)
[Rh(COD)($PePy_2$)](BF_4) (**8**)[d]	rt	1606, 1593	1606, 1596	8.39 (2)	4.6 (4)	24.93 (145.2)
	−90			(a) 8.40 (1), 8.18 (1)	(a) 5.1 (1), 4.7 (2), 4.2 (1)	(a) 24.0 (146)
				(b) 8.40 (2)	(b) 4.7 (2), 3.2 (2)	(b) 28.2 (140)

[a] The number in parentheses corresponds to the number of protons for each signal. [b] Acetone-d_6. [c] $CDCl_3$. [d] CD_2Cl_2. [e] Two isomers observed in solution, being (a) the major and (b) the minor.

Scheme 1. Exchange Outline for Complex 1.



Scheme 2. Equilibrium between Two Isomers of Complex 3.



(the usual separation in cis dicarbonyl complexes is higher, typically 50−70 cm^{-1}).[11]

In the IR spectrum of **3** in the solid state, the presence of only one ν_{Py}(CN) band, at a frequency higher than 1600 cm^{-1}, indicates that both Py groups of the $PePy_2$ ligand are coordinated. In CH_2Cl_2 solution, the IR spectrum of **3** shows a quite broad ν(CO) band at 2011 cm^{-1} with a much less intense shoulder at about 1980 cm^{-1}, suggesting the presence of different isomers or conformers in solution. This is confirmed by the presence of two doublets in a 1:0.22 ratio in the ^{31}P spectrum at room temperature (Table 1). Their similarity in chemical shifts and coupling constants suggests that they correspond to the trans and cis isomers depicted in Scheme 2. Both isomers are also observable in the ^{1}H spectrum. In each of them, the two Py groups are inequivalent, in agreement with the proposed structures. The H^6 chemical shifts indicate that all the Py groups are coordinated. The low solubility of the product precluded dissolution of **3** at low temperature in order to determine whether the cis isomer, found in the solid state, corresponds to the major or to the minor isomer in solution. However, the IR spectrum suggests that the trans isomer (for which only one ν(CO) is expected) is the predominant compound in solution.

An X-ray study of the compound was undertaken. The compound crystallizes in space group $P2_1/n$ with unit cell parameters $a = 12.652(3)$ Å, $b = 26.107(7)$ Å, $c = 16.753(6)$ Å, $\beta = 93.22(3)°$, and $Z = 4$. Although the refinement of the data could not be taken to acceptable values, there was no doubt that the structure is similar to that reported for the complex $[Pd_2(C_6Cl_2F_3)_2\{PePy_2\}_2](BF_4)_2$ with Rh−CO in place of Pd−$C_6Cl_2F_3$.[9] Thus the structure corresponds to that at left in Scheme 2.

Diene Complexes. The complexes with PePy must necessarily be square planar, and accordingly [Rh(TFB)(PePy)](PF_6) (**4**) and [Rh(COD)(PePy)](BF_4) (**5**) in the solid state show only signals of coordinated Py groups in their IR spectra. Complexes with $PePy_2$ can be either square planar or pentacoordinated, and indeed both situations are observed, depending on the diene. The IR spectra of [Rh(NBD)($PePy_2$)](PF_6) (**6**) and [Rh(TFB)-($PePy_2$)](PF_6) (**7**) show only bands due to coordinated Py; hence the complexes are pentacoordinated. However, since the IR spectrum of [Rh(COD)($PePy_2$)](BF_4) (**8**) shows two ν(CN) bands, one due to coordinated Py and one due to uncoordinated Py, **8** must be a square-planar complex with a pendant Py group.

The structure of **6** was ascertained by X-ray diffraction methods and is shown in Figure 1. Selected bond distances and angles are given in Table 2. The geometry of **6** can be described as a sort of piano stool, with the norbornadiene ligand forming the seat, or as a very distorted TBP. The P atom and one olefinic bond are almost trans, with an angle M1−Rh−P of 161.8° [M1 being the midpoint of C(1)−C(6)]. The other olefinic bond is coordinated in the plane defined by N(1), N(2), and the rhodium center, the equatorial plane of the TBP structure. The π-backbonding in the equatorial plane is stronger than that in the axial position, as indicated by the shorter Rh−C(olefinic) and longer C−C(olefinic) bonds for the equatorial alkene when compared with those in the axial position. This effect is usually found in pentacoordinated norbornadiene complexes of rhodium(I)[12,13] and agrees with calculations for pentacoordinated d^8 com-

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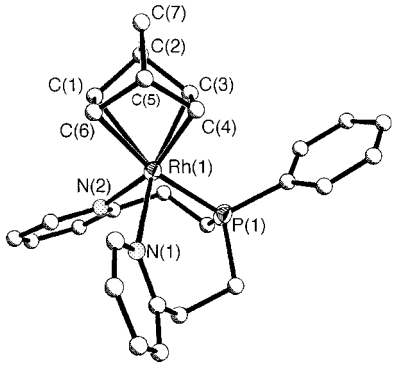

Figure 1. Molecular structure of complex **6** showing the labeling scheme. The PF_6^- anion, the molecule of CH_2Cl_2, and all hydrogens have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **6**

Rh(1)−C(4)	2.072(2)	C(4)−Rh(1)-N(2)	161.74(8)
Rh(1)−C(3)	2.095(2)	C(3)−Rh(1)-N(2)	124.57(9)
Rh(1)−N(2)	2.190(2)	C(4)−Rh(1)-P(1)	100.06(7)
Rh(1)−P(1)	2.2579(5)	C(3)−Rh(1)-P(1)	92.99(6)
Rh(1)−C(6)	2.259(2)	N(2)−Rh(1)-P(1)	89.48(4)
Rh(1)−C(1)	2.279(2)	C(4)−Rh(1)-C(6)	66.44(9)
Rh(1)−N(1)	2.382(2)		
C(3)−Rh(1)-C(6)	77.59(9)	C(6)−Rh(1)-C(1)	34.74(8)
N(2)−Rh(1)-C(6)	103.89(7)	C(4)−Rh(1)-N(1)	104.56(8)
P(1)−Rh(1)-C(6)	166.42(6)	C(3)−Rh(1)-N(1)	144.50(9)
C(4)−Rh(1)-C(1)	77.54(9)	N(2)−Rh(1)-N(1)	90.73(6)
C(3)−Rh(1)-C(1)	63.93(9)	P(1)−Rh(1)-N(1)	90.69(4)
N(2)−Rh(1)-C(1)	86.01(7)	C(6)−Rh(1)-N(1)	91.46(7)
P(1)−Rh(1)-C(1)	147.32(7)	C(1)−Rh(1)-N(1)	121.68(8)

pounds.[14] The bite angle found for the NBD ligand is 69.3°. Each of the pairs of the arms of the $PePy_2$ ligand has a bite angle of ca. 90° at rhodium, and each six-membered PN−Rh ring adopts a boat conformation. Both boats have the same orientation, decreasing the steric interaction between the Py groups. In this conformation, the Py rings are forced to form very different angles with respect to the equatorial plane of the TBP and very different Rh−N distances (2.190(2) Å Rh−N(2) and 2.382(2) Å Rh−N(1)). These distances are slightly longer than others found in analogous Rh(I) complexes containing NBD as a ligand.[12]

Behavior of Complexes 4−8 in Solution. The solution IR spectra of compounds **4**−**7** indicate that these complexes retain in solution the same structures as in the solid state, with all the Py groups coordinated, i.e., square planar for **4** and **5** and pentacoordinated for **6** and **7**. The IR spectrum of compound **8** in solution shows bands at 1596 cm^{-1} (noncoordinated Py) and at 1608 cm^{-1} (broad band, coordinated Py). In fact, since the NMR spectra show that, in solution, **8** is a mixture of two isomers (see below), the IR data imply only that one of them is square planar with a pendant Py.

In accord with the fast conformational change found for **1** and **2** and for related complexes,[6,9] $[Rh(TFB)(PePy)](PF_6)$ (**4**) shows, even at low temperature, equivalence for the protons of each coordinated double bond, the methylenic protons of the PePy ligand, and the two pairs of fluorine atoms. The same applies to $[Rh(COD)(PePy)](BF_4)$ (**5**).

Another process is observed: the exchange of the olefinic protons trans to P and trans to N. This phenomenon is well-known and has been extensively studied for rhodium(I) pyrazolylborate complexes and more recently for other bi- and tridentate nitrogen-containing ligands.[12,15] It has been proposed to occur by a Berry mechanism in pentacoordinated intermediates formed by coordination of pendant arms of the ligands, coordinating anions such Cl^-, or coordinating solvents.

Complexes **6** and **7** show only one sharp doublet in their ^{31}P NMR spectra at all temperatures. Their ^1H NMR spectra show only signals for one pentacoordinated isomer at all temperatures studied. At room temperature they show equivalence of the olefinic protons and the Py rings. At −90 °C, all the signals are in coalescence for **6**, but for **7**, they are below coalescence and two inequivalent Py rings, both coordinated, are observed. At the same time, all the protons (in the ^1H spectrum) and all the F atoms (in the ^{19}F spectrum) of the TFB ligand appear inequivalent. In other words, the low-temperature ^1H and ^{19}F NMR spectra of **7** correspond to the situation expected from the structure observed in the solid, while the room-temperature spectrum requires (i) fast site exchange of the two double bonds and (ii) fast inversion of the boat conformation of the metallacycles involving the Py groups. Each movement alone cannot produce all the equivalencies observed. For instance, the equivalence of the fluorines by pairs is produced by any of them. On the contrary, (i) would produce equivalence of olefinic protons by pairs in two different double bonds, whereas (ii) would produce equivalence by pairs of signals from the same double bond, but total equivalence requires the occurrence of both processes. The exchange is outlined in Scheme 3. The rotation motion (i) is represented in a box for each conformation and exchanges even or odd olefinic protons between them. The conformational change means movement from one box to the other (i.e., **C** to **C′**, **D** to **D′**, etc.) and makes equivalent the olefinic protons of each double bond.

At higher temperatures (−88 °C), the boat inversion in **7** broadens all the signals on the spectrum and eventually leads to the coalescence of the H^6 signals of the Py groups at T_c = −69 °C, which corresponds to a $\Delta G^{\ddagger}$ of 36.9 kJ mol^{-1} (k = 1560 s^{-1}).[16] The process is also observable by ^{19}F NMR, where the fluorine signals become equivalent two by two in the same temperature range. Also in this temperature interval, the exchange of the coordination sites of the TFB ligand by rotation starts to be observed and the olefinic signals coalesce to one at room temperature. For **6**, the fluxional processes are faster and only the averaged signals are observed in the temperature window of the solvent (acetone-d_6). Thus, again a fast conformational change is found compared to the case of the complexes with $P(bzN)_n$,[10] despite the apparently more crowded situation in a pentacoordinated structure.

The complex $[Rh(COD)PePy_2](BF_4)$ (**8**) behaves quite differently. At −90 °C, its ^{31}P NMR spectrum reveals the existence of two different isomers in a 1.5:1 ratio, which are also seen in the ^1H NMR spectrum (Table 1). A COSY experiment allowed us to assign the signals, which correspond to one square-planar (major) and one trigonal-bipyramidal (minor) isomer (Figure 2). This assignment is further supported by a $^{31}P-^1H$ correlation experiment, which shows the couplings of each olefinic proton signal with its corresponding ^{31}P signal and also agrees with

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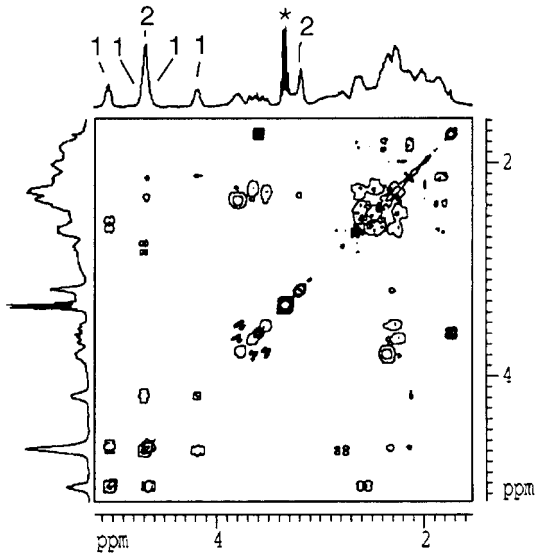
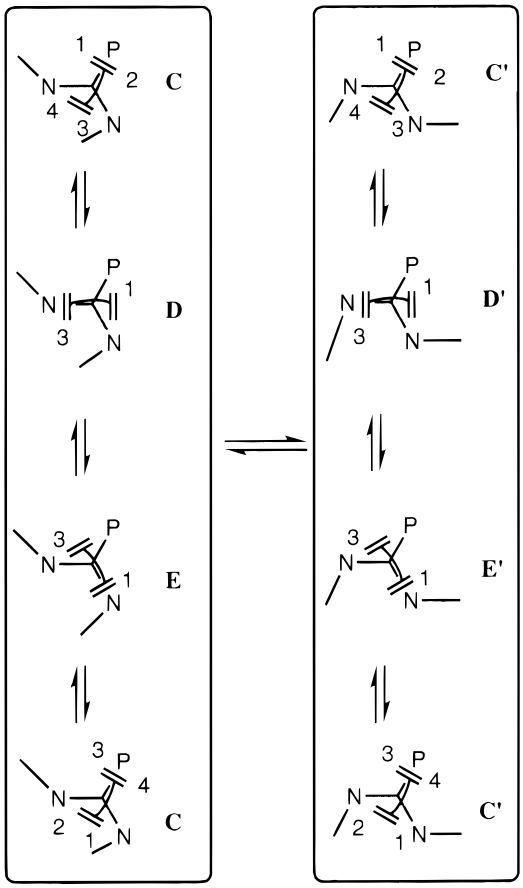


Figure 2. COSY spectrum of **8** at −90 °C in CD_2Cl_2: (1) olefinic signals of the square-planar isomer; (2) olefinic signals of the trigonal-bipyramidal isomer. (*) solvent signal.

Scheme 3. Exchanges in **7**.[a]



[a] The Rotation of the Diolefin Exchanges the Olefinic Protons 1 with 3 and 2 with 4. The simultaneous conformational changes of the chelated rings allow for the exchange of the four olefinic protons. The different conformations of the metallacycles are indicated by the different orientations of the substituents at the N atoms.

the IR spectrum described before. Furthermore, a $^1H-^{13}C$ correlation experiment (Figure 3) shows that the olefinic signal at 4.7 ppm is in effect the result of three different protons overlapping, as it is related to three ^{13}C signals at 77.8, 103.0, and 103.8 ppm, while the olefinic signals at 5.1, 4.2, and 3.2

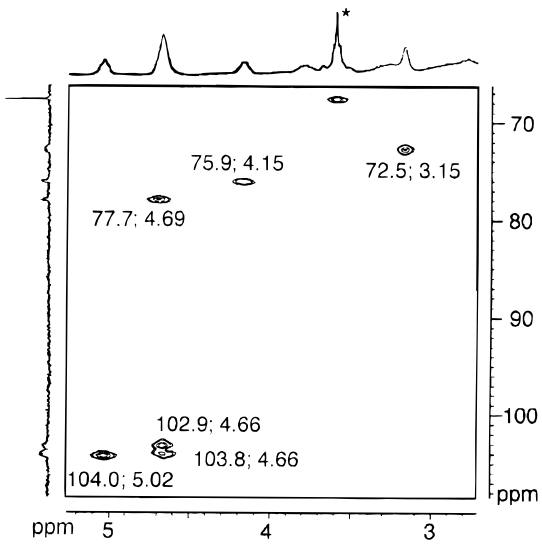


Figure 3. $^{13}C-^1H$ correlation spectrum in CD_2Cl_2 at −90 °C (only olefinic signals shown): (*) solvent.

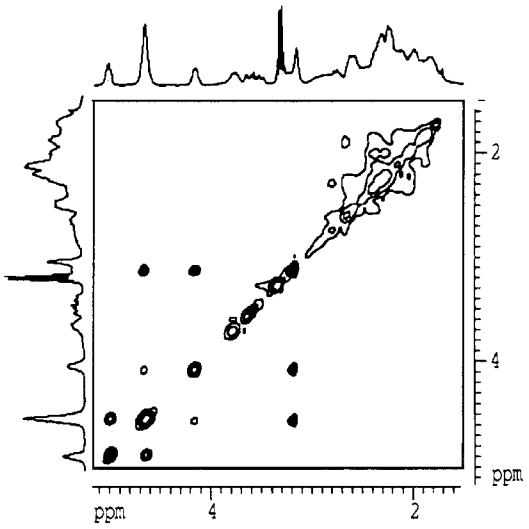


Figure 4. EXSY NMR spectrum of **8** at −90 °C in CD_2Cl_2.

ppm correlate with signals at 104.0, 75.9, and 72.5 ppm, respectively.[17] This is again in agreement with the proposed assignment.

In the minor isomer (pentacoordinated), the two Py groups are equivalent, and only two olefinic signals are observed due to the fast conformational change on the chelated rings, as previously described for compound **6**. The equilibrium between these isomers has been studied by an EXSY experiment at −90 °C (Figure 4). It shows that each Py group of the square-planar isomer is exchanging with the Py groups of the pentacoordinated isomer and also that the olefinic protons of both complexes are exchanging. Particularly informative is the fact that the olefinic signal of the pentacoordinated complex at 3.2 ppm does not exchange with the olefinic proton signal at 5.1 ppm while it gives strong cross-peaks with the olefinic proton signals at 4.2 and 4.7 ppm. This means that each double bond of the square-planar complex exchanges with just one double bond of the trigonal-bipyramidal isomer. Since an exchange of the Py groups on **6** is possible without moving the coordinated phosphorus (in the trigonal-bipyramidal structure both Py groups are in

(17) We are grateful to an anonymous reviewer for suggesting this experiment.

equatorial positions), the slow fluxionality of the trigonal-bipyramidal structure does not affect the Py exchange rate, which is only related to the rate of exchange between the square-planar and bipyramidal-trigonal structures. Hence, the equilibrium keeps one olefin trans to the phosphorus and the other trans to the nitrogen. This implies that the rotation of the olefin on the pentacoordinated complex is slower than the equilibrium between square-planar and trigonal-bipyramidal isomers.

This exchange mechanism is consistent with the evolution of the signals during the variable-temperature experiments. With an increase in temperature, a coalescence is observed ($T_c = -50$ °C). This affects all the olefinic signals in such a way that each olefin of the square-planar isomer coalesces with just one of the trigonal-bipyramidal isomers. Between −40 and 0 °C, two olefinic signals are observable. When the temperature is raised to 10 °C, the two olefinic signals that were observable at 0 °C reach a new coalescence and become equivalent at 50 °C. This second coalescence is related to the site exchange of the olefin (axial−equatorial) in the trigonal-bipyramidal structure.

Simultaneously with the first coalescence in ^{1}H NMR, the ^{31}P NMR spectrum shows the coalescence of the two signals that correspond to the square-planar and the pentacoordinated isomers. Line shape analysis of the ^{31}P signals at −61 °C gives a value of $k_{ex} = 70\ s^{-1}$ ($\Delta G^{\ddagger} = 43.8$ kJ mol^{-1}).[18]

This exchange pattern confirms the assignment of the isomers and constitutes a rare example of equilibrium in which the fluxionality in a pentacoordinated intermediate is slower than the equilibrium between penta- and tetracoordinate complexes.

Experimental Section

General Methods and NMR Techniques. All reactions were carried out under N_2. Solvents were distilled using standard methods. The complexes $[Rh_2(\mu\text{-Cl})_2(1,5\text{-COD})_2]$[19] and $[Rh_2(\mu\text{-Cl})_2(TFB)_2]$,[20] $[Rh_2(\mu\text{-Cl})_2(CO)_4]$, the ligand $PePy_2$, and $TlBF_4$ were prepared by published methods.[21−23]

IR spectra were recorded on a Perkin-Elmer FT 1720 X spectrophotometer. Combustion CHN analyses were made on a Perkin-Elmer 2400 CHN microanalyzer. ^{1}H NMR (300.16 MHz), ^{19}F NMR (282.4 MHz), and ^{31}P NMR (121.4 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with a VT-100 variable-temperature probe. Chemical shifts are reported in ppm from tetramethylsilane (^{1}H), CCl_3F (^{19}F), or H_3PO_4 (85%) (^{31}P), with positive shifts downfield, at ambient probe temperature unless otherwise stated. NOESY spectra were recorded in the phase-sensitive mode, using the average of the relaxation times as mixing time. The ^{1}H−^{13}C correlation spectra were recorded in the inverse mode, with a HMQC sequence with BIRD selection and GARP decoupling during acquisition.

Synthesis of the Complexes. (a) [RhCl(CO)(PePy$_2$)] (1). A solution of $PePy_2$ (161 mg, 0.50 mmol) in CH_2Cl_2 (5 mL) was saturated with CO by bubbling for 5 min. Then $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ (97 mg, 0.25 mmol) was added. After 30 min of stirring, *n*-hexane (12 mL) was added. The complex precipitated as a yellow powder, which was filtered off and vacuum-dried. Attempts at washing the solid with *n*-hexane or diethyl ether led to the formation of oils. Yield: 219 mg (89%). Anal. Calcd for $C_{21}H_{21}ClN_2OPRh$: C, 51.82; N, 5.76; H, 4.35. Found: C, 51.62; N, 5.68; H, 4.26. ^{1}H NMR (acetone-d_6, rt (room temperature)): δ 8.79 (m, 2H); δ 7.99−7.96 (m, 2H); δ 7.77 (m, 2H); δ 7.45 (m, 3H); δ 7.38 (m, 2H); δ 7.26 (m, 2H); δ 3.25 (m, 4H); δ 2.59 (m, 2H); δ 2.32 (m, 2H). ^{31}P NMR (acetone-d_6, rt): δ 44.0 (d, $J_{RhP} = 161.5$ Hz). IR (Nujol mull, cm^{-1}): 1974 vs, ν(CO); 1587 m, 1606 m, ν(CN). IR (CH_2Cl_2, cm^{-1}): 1991 vs, ν(CO); 1596 m, 1608 m, ν(CN).

(b) [RhI(CO)(PePy$_2$)]·0.5CH$_3$COCH$_3$ (2). To a solution of $[Rh_2(CO)_2(PePy_2)_2](BF_4)_2$ (300 mg, 0.28 mmol) in acetone (15 mL) was added sodium iodide (340 mg, 2.28 mmol). After 1 h, the solution was filtered, the acetone was evaporated to 2 mL, and ethanol (10 mL) was added. The compound was crystallized by cooling to −20 °C as brown crystals, which were filtered off and vacuum-dried. Yield: 275 mg (80%). Anal. Calcd for $C_{22.5}H_{24}IN_2O_{1.5}PRh$: C, 44.50; N, 4.61; H, 3.98. Found: C, 44.48; N, 4.58; H, 3.93. ^{1}H NMR ($CDCl_3$, rt): δ 8.90 (m, 2H); δ 7.78, (m, 2H); δ 7.60 (m, 2H); δ 7.53−7.09 (m, 7H); δ 3.15 (m, 4H); δ 2.43 (m, 2H); δ 2.24, (m, 2H). ^{31}P NMR ($CDCl_3$, rt): δ 41.8 (d, $J_{Rh-P} = 168.4$ Hz). IR (Nujol mull, cm^{-1}): 1966 vs, 1730 s, ν(CO); 1605 m, 1593 s, ν(CN). IR (CH_2Cl_2, cm^{-1}): 1987 vs, ν(CO); 1608 m, 1595 m, ν(CN).

(c) [Rh$_2$(CO)$_2$(PePy$_2$)$_2$](BF$_4$)$_2$ (3). To a solution of $[Rh_2(\mu\text{-Cl})_2(COD)_2]$ (343 mg, 0.695 mmol) in acetone (20 mL) were added $PePy_2$ (445 mg, 1.39 mmol) and $TlBF_4$ (405 mg, 1.39 mmol). The solution was stirred during 1 h, filtered, and allowed to stir under CO for 2 h. During this time, the complex, a pale yellow product, crystallized. The addition of diethyl ether (15 mL) completed the precipitation. The product was filtered off, washed with diethyl ether, and vacuum-dried. Yield: 626 mg (90%). Anal. Calcd for $C_{42}H_{42}B_2F_8N_4O_2P_2Rh_2$: C, 46.87; H, 3.77; N, 5.20. Found: C, 46.81; H, 3.72; N, 5.16. ^{1}H NMR (CD_2Cl_2, rt) for major isomer, *trans*-$[Rh_2(CO)_2(PePy_2)_2](BF_4)_2$: δ 8.76 (m, 1H); δ 7.81 (m, 1H); δ 8.04 (m, 2H); δ 7.98 (m, 1H); δ 7.87 (m, 2H); δ 7.56 (m, 4H); δ 7.43 (m, 1H); δ 7.14 (m, 1H); δ 4.96 (m, 1H); δ 3.73 (m, 1H); δ 3.48 (m, 2H); δ 3.06 (m, 1H); δ 2.58 (m, 2H); δ 2.28 (m, 1H). ^{1}H NMR for minor isomer, *cis*-$[Rh_2(CO)_2(PePy_2)_2](BF_4)_2$: δ 8.66 (m, 1H); δ 7.72 (m, 1H); δ 8.22 (m, 2H); δ 8.07 (m, 2H); δ 7.8 (m, 1H); δ 7.64 (m, 2H); δ 7.55 (m, 1H); δ 7.45 (m, 2H); δ 7.01 (m, 1H); δ 4.43 (m, 1H); δ 4.21 (m, 1H); δ 2.34 (m, 2H); 2.94 (m, 1H); δ 2.76 (m, 1H); δ 2.35 (m, 1H); δ 2.20 (m, 1H). ^{31}P NMR (CD_2Cl_2, rt): major isomer δ 45.7 (d, $J_{Rh-P} = 148.5$ Hz); minor isomer δ 47.3 (d, $J_{Rh-P} = 148.2$ Hz). IR (Nujol mull, cm^{-1}): 2002 vs, 1978 vs, ν(CO); 1606 s, ν(CN). IR (CH_2Cl_2, cm^{-1}): 2011 vs, 1980 sh, ν(CO).

(d) [Rh(TFB)(PePy)](PF$_6$) (4). To a stirred suspension of $[Rh_2(\mu\text{-Cl})_2(TFB)_2]$ (100 mg, 0.137 mmol) in acetone (10 mL) were added PePy (88 mg, 0.274 mmol) and $AgNO_3$ (48 mg, 0.274 mmol). After 24 h, the precipitate of AgCl was filtered off, the acetone was evaporated, and ethanol (10 mL) was added. Upon the addition of NH_4PF_6 (88 mg, 0.536 mmol) dissolved in the smallest amount of ethanol, the product precipitated as an orange powder, which was filtered off, washed with 2 mL of $CHCl_3$, and vacuum-dried. Yield: 153 mg (75%). Anal. Calcd for $C_{31}H_{24}F_{10}NP_2Rh$: C, 48.65; N, 1.83; H, 3.16. Found: C, 48.59; N, 2.02; H, 3.24. ^{1}H NMR (acetone-d_6, rt): δ 8.67 (m, 1H); δ 7.93 (m, 2H); δ 7.72−7.41 (m, 11H); δ 5.99 (m, 2H); δ 5.70 (br, 2H); δ 3.99 (m, 1H); δ 3.90 (m, 1H); δ 3.65 (br, 2H); δ 2.66 (m, 2H). ^{19}F NMR (acetone-d_6, rt): δ −147.0 (m, 2F); δ −160.0 (m, 2F); δ −71.0 (d, $J_{P-F} = 708$ Hz, 6F). ^{31}P NMR (acetone-d_6, rt): δ 34.0 (d, $J_{Rhp} = 166.9$). IR (Nujol mull, cm^{-1}): 1609 s, ν(CN). IR (CH_2Cl_2, cm^{-1}): 1602 s, ν(CN).

(e) [Rh(COD)(PePy)](BF$_4$) (5). To a solution of $[Rh_2(\mu\text{-Cl})_2(1,5\text{-COD})_2]$ (120 mg, 0.243 mmol) in THF (20 mL) was added $AgBF_4$ (94.7 mg, 0.487 mmol). The mixture was stirred for 30 min, and the precipitate of AgCl was filtered off. PePy (142 mg, 0.487 mmol) was added to the solution. The mixture was stirred for 1 h. Concentration of the clear solution yielded yellow crystals, which were filtered off and vacuum-dried. Yield: 260 mg (90%). Anal. Calcd for $C_{27}H_{30}BF_4NPRh$: C, 55.04; N, 2.38; H, 5.13. Found: C, 55.11; N, 2.23; H, 5.12. ^{1}H NMR (acetone-d_6, rt): δ 8.87 (m, 1H); δ 7.80 (m, 1H); δ 7.63 (m, 5H); δ 7.44 (m, 6H); δ 7.32 (m, 1H); δ 5.26, (m, 2H); δ 4.01 (m, 2H); δ 3.79 (m, 2H); δ 2.83, (m, 2H); δ 2.55 (m, 4H); δ 2.24 (m, 4H). ^{31}P NMR (acetone-d_6, rt): δ 34.2 (d, $J_{Rh-P} = 148.9$ Hz). IR (KBr pellet, cm^{-1}): 1606 s, ν(CN).

(f) [Rh(NBD)(PePy$_2$)](PF$_6$)·CH$_2$Cl$_2$ (6). To a stirred suspension of $[Rh_2(\mu\text{-Cl})_2(NBD)_2]$ (152 mg, 0.329 mmol) in acetone (15 mL) were added $PePy_2$ (211 mg, 0.659 mmol) and $TlBF_4$ (192 mg, 0.659 mmol). After 1 h, the TlCl was filtered off, the solvent was evaporated, and ethanol (10 mL) was added. Upon addition of NH_4PF_6 (536 mg, 3.28 mmol) dissolved in the smallest amount of ethanol, the product

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precipitated as a yellow sticky solid. The ethanol was filtered off and the solid was washed twice with diethyl ether (15 mL each). The yellow powder was filtered off and vacuum-dried. The compound was recrystallized by slow diffusion in CH_2Cl_2/hexane. Yield: 220 mg (85%). Anal. Calcd for $C_{28}H_{31}Cl_2F_6N_2P_2Rh$: C, 45.12; N, 3.76; H, 4.19. Found: C, 45.04; N, 3.74; H, 4.22. ^{1}H NMR (acetone-d_6, rt): δ 8.87 (m, 2H); δ 7.94 (m, 2H); δ 7.57−7.37 (m, 9H); δ 3.43 (m, 2H); δ 3.70 (s, 2H); δ 3.43 (m, 4H); δ 2.71 (m, 2H); δ 2.40 (m, 2H); δ 2.17 (m, 2H); δ 1.22 (s, 2H). ^{31}P (acetone-d_6, rt): δ 35.5 (d, J_{Rh-P} = 144.7 Hz). IR (Nujol mull, cm^{-1}): 1600 s, ν(CN).

(g) [Rh(TFB)(PePy$_2$)](PF$_6$) (7). To a stirred suspension of [Rh$_2$(μ-Cl)$_2$(TFB)$_2$] (100 mg, 0.137 mmol) in acetone (10 mL) were added PePy$_2$ (91 mg, 0.284 mmol) and TlBF$_4$ (82 mg, 0.284 mmol). After 1 h, the TlCl was filtered off, the acetone was evaporated, and ethanol (10 mL) was added to the yellow oil. After the addition of NH_4PF_6 (223 mg, 1.37 mmol) dissolved in the smallest amount of ethanol, the product precipitated as a yellow powder, which was filtered off, washed with ethanol, and vacuum-dried. Yield: 180 mg (83%). Anal. Calcd for $C_{32}H_{27}BF_8N_2PRh$: C, 52.20; N, 3.80; H, 3.70. Found: C, 52.25; N, 3.71; H, 3.66. ^{1}H NMR (acetone-d_6, rt): δ 8.94 (m, 2H); δ 8.00 (m, 2H); δ 7.65−7.40 (m, 9H); δ 5.46 (m, 2H); δ 3.57 (m, 2H); δ 3.45 (br, 4H); δ 2.80 (m, 2H); δ 2.54 (m, 2H); δ 2.22 (m, 2H). ^{19}F NMR (acetone-d_6, rt): δ −148 (m, 2F); δ −161.5 (m, 2F); δ −71.5 (d, 6F, J_{P-F} = 708 Hz). ^{31}P NMR (acetone-d_6, rt): δ 43.52 (d, J_{Rh-P} = 146.32 Hz). IR (Nujol mull, cm^{-1}): 1604 m, ν(CN). IR (CH_2Cl_2, cm^{-1}): 1608 m, ν(CN).

(h) [Rh(COD)(PePy$_2$)](BF$_4$) (8). To a stirred solution of [Rh$_2$(μ-Cl)$_2$(1,5-COD)$_2$] (194 mg, 0.393 mmol) in THF (20 mL) was added $AgBF_4$ (152 mg, 0.785 mmol). After 2 h, the precipitate of AgCl was filtered off and PePy$_2$ (265 mg, 0.827 mmol) was added. The THF was evaporated to 2 mL, and the complex was precipitated by addition of diethyl ether (15 mL). The yellow powder formed after repetitive washings with ether was filtered off and vacuum-dried. Yield: 410 mg (84%). Anal. Calcd for $C_{27}H_{29}BF_4N_2PRh$: C, 54.39; N, 4.53; H, 5.38. Found: C, 54.24; N, 4.51; H, 5.48. ^{1}H NMR (acetone-d_6, rt): δ 8.76 (d, J = 5.1 Hz, 2H); δ 7.79 (m, 2H); δ 7.62 (m, 2H); δ 7.4, (m, 5H); δ 7.26 (m, 2H); δ 4.7 (br, 4H); δ 3.4 (br, 4H); δ 2.60−2.3 (br, 12H). ^{31}P NMR (acetone-d_6, rt): δ 26.6 (d, J_{Rh-P} = 145.7 Hz). IR (KBr pellet, cm^{-1}): 1606 s, 1593 s, ν(CN). IR (CH_2Cl_2, cm^{-1}): 1606 s, 1596 s, ν(CN).

Crystal Structure Determination of 6·CH$_2$Cl$_2$. Crystals of **6·CH$_2$Cl$_2$** suitable for X-ray diffraction were obtained through recrystallization of **6** by slow diffusion in dichloromethane/hexane A yellow crystal (0.30 × 0.25 × 0.25 mm) was coated with high-vacuum grease and mounted on a Siemens SMART diffractometer under a stream of N_2 at 173 K. Crystallographic data are summarized in Table 3. An empirical absorption correction (SADABS) was applied.[24] The structure was solved by direct methods and refined on all F^2 data using the SHELX suite of programs on a Silicon Graphics Indy computer.[25] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms H(1)−H(6)- were located in the electron density difference map, assigned isotropic displacement parameters, and refined without positional constraints. All other hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Refinement proceeded smoothly to give the residuals shown in Table 3. Complex neutral-atom scattering factors were used.[26]

Table 3. Crystallographic Data for **6**

empirical formula	$C_{28}H_{31}Cl_2F_6N_2P_2Rh$
fw	745.3
temp	173 K
wavelength	0.710 73 Å
space group	$P2_1/n$
unit cell dimens	a = 8.455(1) Å
	b = 18.068(3) Å
	c = 19.729(3) Å
	β = 99.658(3)°
	V = 2971.1(8) Å^3
Z	4
density (calcd)	1.666 Mg/m^3
μ(Mo Kα)	0.923 mm^{-1}
R indices [for 5468 reflns with $I > 2\sigma(I)$]	R1 = 0.0264, wR2 = 0.0624
R indices (for all 6793 data)	R1 = 0.0382, wR2 = 0.0660

Acknowledgment. The Dirección General de Investigación Científica y Técnica (Projects PB96-0363 and SB95-BOZ67791015) and the Junta de Castilla y León (Project VA40/96) are gratefully acknowledged for financial support and fellowships to K.S. and M.A.A.

Supporting Information Available: An X-ray crystallographic file, in CIF format, for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990634A

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