Chiral Ruthenium Complexes with *P,N*-Ligands Derived from (*S*)-Proline

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Received October 18, 2000

$[Ru_2(OAc)_4]$ cleanly reacts with 2-(*S*)-diphenylphosphinomethylpyrrolidine (**PPro**) and 2-(*S*)-diphenylphosphinomethyl-*N*-methylpyrrolidine (**PProMe**) to give *trans,trans,trans*-$[Ru(OAc)_2(PPro)_2]$ (**2**) and $[Ru(OAc)_2(PProMe)_2]$, respectively, which possess stereogenic nitrogen atoms. The latter complex exists as the *cis-P,P-cis-P,N-*(Δ)-stereoisomer (Δ-**3**) in THF and as the (Λ)-stereoisomer (Λ-**5**) with *cis-P,P-trans-N,N* coordination geometry in MeOH. Formation of *N*-based stereocenters occurs selectively, and complexes **2**, **3**, and **5** are present as single epimers in solution and in the solid state. Thermolysis of Δ-**3** in boiling dioxane affords (Δ)- and (Λ)-stereoisomers of the carbene ruthenium complex (**7**), due to facile dehydrogenation of the *N*-Me groups of the ligand.

Introduction

Ruthenium complexes with *P,N*-chelating ligands demonstrate remarkable structural diversity. Thus, compounds displaying *P,P-cis, N,N-cis*;[1−3] *P,P-cis, N,N-trans*;[4,5] all *cis*;[5,6] and all *trans*[7,8] coordination geometries (Chart 1) have been prepared and characterized by X-ray diffraction.

Octahedral metallocomplexes featuring three or at least two noncoplanar chelate cycles are chiral and usually exist as racemic mixtures of (Δ)- and (Λ)-enantiomers (Chart 2). Application of chiral ligands, however, may lead to the selective formation of one diastereomer. For instance $[Ru(OAc)_2(BINAP)]$ has the (Δ,*R*)- or (Λ,*S*)-configuration, whereas the corresponding (Λ,*R*)- or (Δ,*S*)-epimer was not obtained.[9]

Chiral aminophosphines prepared from (*S*)-proline (**1a**,**b**, Chart 3) were used as chiral auxiliaries in Pd-catalyzed asymmetric allylation[10] and Grignard cross coupling.[11] To the best of our knowledge no structurally characterized metallocomplexes of these ligands have been reported. Coordination of the aminophosphines **1a**,**b** to a metal results in the formation of stereogenic nitrogen centers incorporated into [3.3.0] bicyclic systems which are either *cis*- or *trans*-fused (Chart 3) and

Chart 1

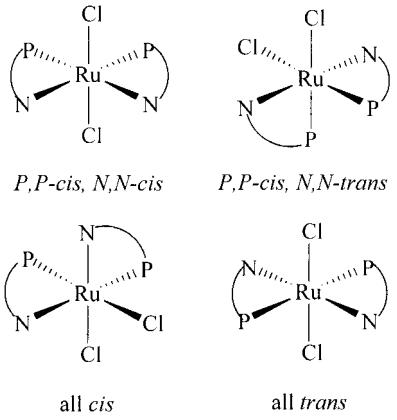

Chart 2

can be considered as analogues of *cis*- and *trans*-bicyclooctanes. Since *cis*-C_8H_{14} is thermodynamically more stable than the corresponding *trans*-isomer,[12] preferential formation of metallo complexes possessing type **A** structural fragments with *(S)*-absolute configuration of the nitrogen would be expected.

We now wish to report the structure and properties of chiral Ru complexes prepared from **1a**,**b** and $[Ru_2(OAc)_4]$. We also describe an improved synthesis of ruthenium acetate, by a simple "one-pot" modification of Lindsay's procedure,[13] which results in an increased yield of 70−80% compared to 47% previously reported.

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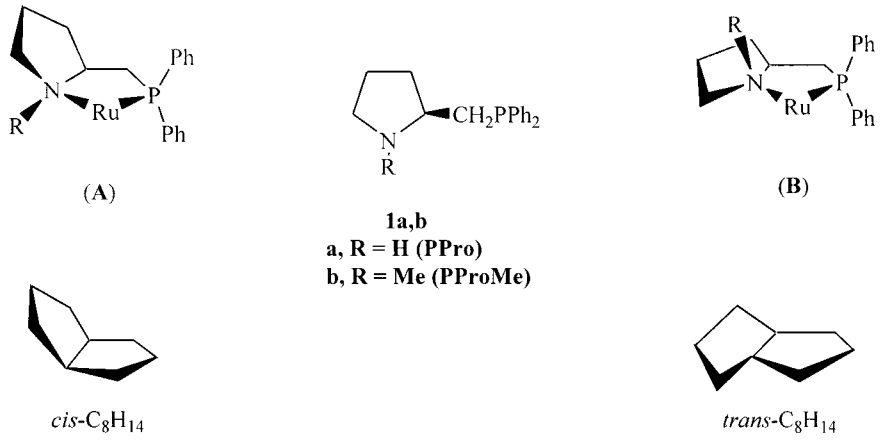
10.1021/om000894w CCC: $20.00
Publication on Web 03/02/2001

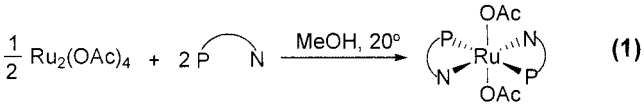
Chart 3



$\Delta G^{o}_{(cis\text{-}C_8H_{14})} - \Delta G^{o}_{(trans\text{-}C_8H_{14})} = -26.8$ kJ/ mol

Results and Discussion

Reaction of PPro with $[Ru_2(OAc)_4]$. X-ray Structure of $[Ru(OAc)_2(PPro)_2]$. Treating a methanol suspension of $[Ru_2(OAc)_4]$ with 2 equiv of PPro leads to the formation of complex **2** (eq 1), along with ca. 5% of unidentified side-products.[14,15] According to ^{31}P NMR spectra, the reaction is complete in 5 min at room temperature.



The complex was isolated in high yield as air-stable yellow crystals (1:1 methanol solvate) which are soluble in CH_2Cl_2, moderately soluble in THF and benzene, and slightly soluble in MeOH and Et_2O. The solid state structure of **2** (1:1 Et_2O solvate) was established by single-crystal X-ray diffraction. An ORTEP plot of the complex is shown in Figure 1; selected bond distances and angles are presented in Table 1.

The octahedral coordination environment of the central Ru atom consists of two *P*,*N*-chelating aminophosphines and a pair of mutually *trans*-monodentate acetates. The two phosphorus atoms are *trans* to each other and lie in the same plane with the two *trans*-nitrogen atoms of the chelates. In such an arrangement the ruthenium is not stereogenic. One of the two bicyclic [3.3.0] systems of **2** is *cis*-fused, whereas the other adopts the thermodynamically less stable *trans*-conformation, presumably due to hydrogen bonding between the coordinated acetate and amino groups (the H(1c)···O(2) and H(2c)···O(4) separations are 1.985 and 2.04 Å, respectively). To form hydrogen bonds with the two mutually *trans*-OAc ligands, one of the two *N*-H protons should lie above while another lies below the P−N−P−N equatorial plane of the molecule; as a result, the two *N*-based stereocenters of the complex possess opposite absolute configurations.

(14) The reaction in THF or CH_2Cl_2 gives **2** along with ca. 30% of unidentified side-products.

(15) Attempts to prepare a 1:1 Ru−**PPro** complex by treating of $[Ru_2(OAc)_4]$ with 1 equiv of **1a** were unsuccessful. A complex mixture of unidentified products, along with traces of **2**, was observed by ^{31}P NMR.

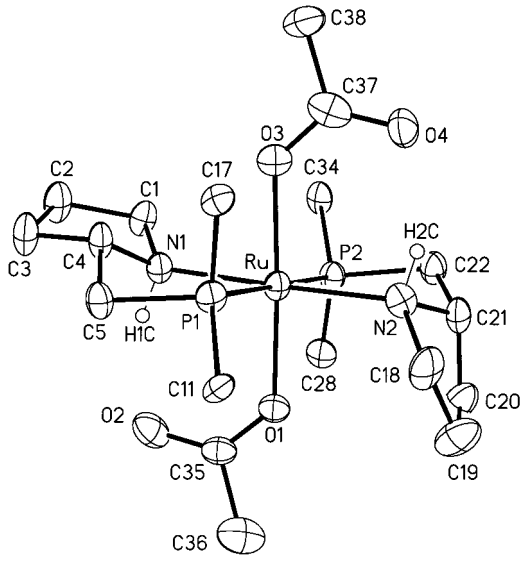


Figure 1. Perspective diagram of **2** with 50% probability ellipsoids. The hydrogen atoms (except for *N*-H) and phenyl carbon atoms (except for *ipso*) are omitted for clarity.

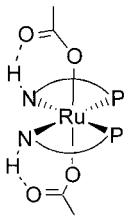
Table 1. Selected Bond Distances (Å) and Angles (deg) for 2·Et_2O

N(1)−Ru	2.142(5)	C(1)−N(1)−Ru	122.9(3)
N(2)−Ru	2.163(5)	C(1)−N(1)−C(4)	103.1(5)
O(1)−Ru	2.098(4)	C(4)−N(1)−Ru	113.7(3)
O(3)−Ru	2.118(4)	C(18)−N(2)−Ru	119.6(4)
P(1)−Ru	2.363(2)	C(18)−N(2)−C(21)	101.4(5)
P(2)−Ru	2.309(2)	C(21)−N(2)−Ru	117.8(4)

The $^{31}P\{^1H\}$ NMR spectrum of **2** in toluene at 20 °C displays a well-resolved AB pattern typical for complexes with two nonequivalent *trans*-phosphine ligands. The lines neither collapsed nor broadened significantly when the spectrum was recorded from −80 to +110 °C. Therefore, it appears that the structure of **2** remains intact in solution, and pseudorotation of chelates, which could proceed via decoordination−inversion of configuration−recoordination of amino groups does not occur or it is slow on the NMR time scale. The lack of fluxional behavior demonstrated by **2** is probably attributable to the strong NH−OAc hydrogen bonding, which not only induces the thermodynamically unfavorable *trans*-fusion of the [3.3.0] bicyclic system, but also makes the whole structure robust.

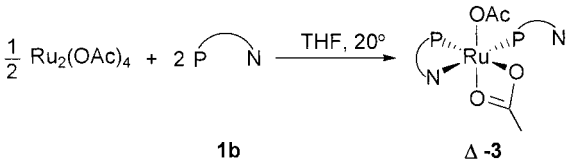
It should be noted that hydrogen bonding alone

cannot explain the presence of a *trans*-fused bicyclic system in **2**. Indeed, amino groups of the hypothetical *cis-P,P, cis-N,N, trans-O,O* isomer could also form hydrogen bonds with two mutually *trans* OAc ligands, but both [3.3.0] ring systems of the molecule would possess *cis*-configuration. Therefore the observed *trans-P,P, trans-N,N* arrangement of chelates in **2** arises despite concomitant formation of the thermodynamically less stable *trans*-fused bicyclic system. Unfortunately the available experimental data do not allow us to ascertain whether the structure of **2** corresponds to the most thermodynamically stable configuration, or **2** is just the kinetic product which possesses rigid structure and therefore is not prone to rearrangement even at elevated temperatures.



Hypothetical *cis*, *cis*, *trans*- $Ru(OAc)_2(PPro)_2$

Reaction of PProMe with $[Ru_2(OAc)_4]$. X-ray Structure of $[Ru(OAc)_2(PProMe)_2]$. Ruthenium acetate readily reacts with 2 equiv of **PProMe** affording complex Δ-**3** selectively (eq 2).[16] According to ^{31}P NMR spectra, the reaction is complete in 5 min at room temperature.



1b **Δ -3** **(2)**

The analytically pure complex was isolated in high yield by crystallization from cyclopentane as a 1:1 C_5H_{10} solvate. The large orange crystals of Δ-**3**·C_5H_{10} are air stable and soluble in common organic solvents. The solid state structure of the complex was established by single-crystal X-ray diffraction. The asymmetric unit of the crystalline Δ-**3**·C_5H_{10} contains two independent molecules of the complex. Although crystallographically important, the difference between the two molecules is chemically insignificant (both are (Δ)-stereoisomers possessing the same spatial arrangement of the atoms and very close values of the corresponding bond lengths and angles). The ORTEP plot (Figure 2) shows only one arbitrarily chosen molecule of the asymmetric unit. The selected bond lengths and angles are given in Table 2.

In contrast to the case for complex **2**, only one of the two aminophosphine ligands of Δ-**3** is *P,N*-chelating, while another is attached to Ru only via phosphorus. The two P atoms are *cis* to each other and lie in the same plane with the coordinated nitrogen. As expected the [3.3.0] bicyclic system of the molecule is *cis*-fused and the *N*-based stereocenter adopts an *(S)*-configuration.

(16) Reaction of $[Ru_2(OAc)_4]$ with 1 equiv of **PPrOMe** afforded a product of unknown structure, which shows a singlet at 87 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The complex was not isolated due to fast decomposition in solution (half-life ca. 6 h in THF at 20 °C), leading to the formation of a mixture of unidentified products.

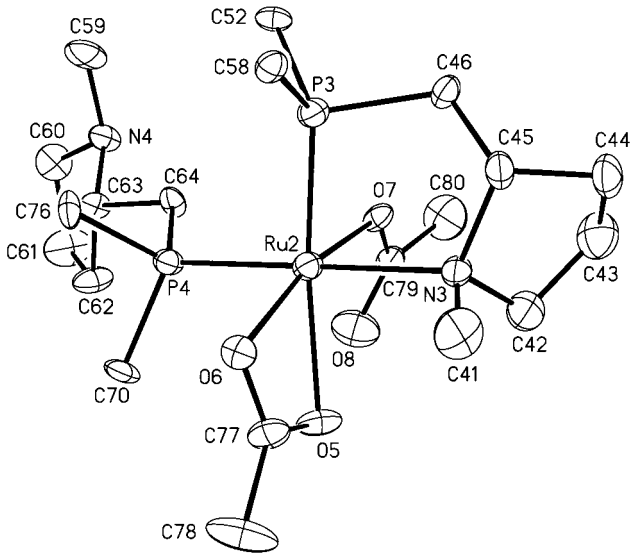
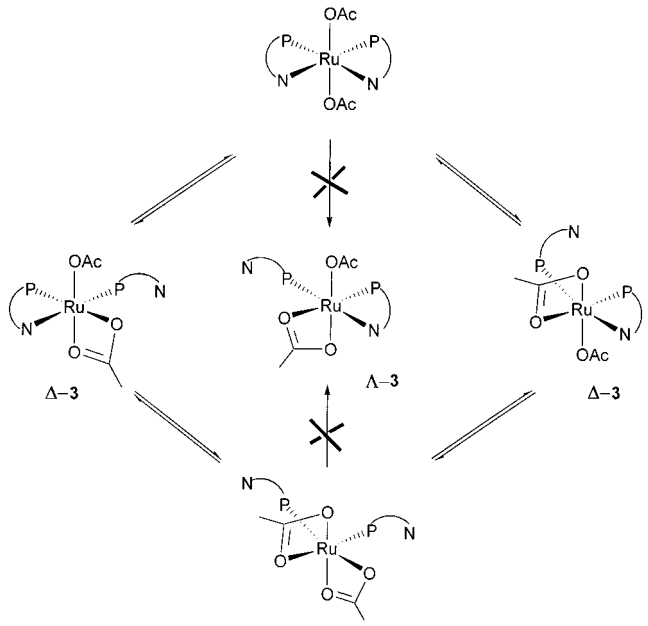


Figure 2. Perspective diagram of Δ-**3** with 30% probability ellipsoids. All hydrogen atoms and non *ipso*-phenyl carbon atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Δ-3·C_5H_{10}

O(5)−Ru(2)	2.214(9)	O(5)−Ru(2)−O(6)	61.0(3)
O(6)−Ru(2)	2.139(8)	C(41)−N(3)−C(42)	111.1(11)
O(7)−Ru(2)	2.062(8)	C(41)−N(3)−C(45)	105.6(11)
N(3)−Ru(2)	2.270(10)	C(41)−N(3)−Ru(2)	111.2(8)
P(3)−Ru(2)	2.207(4)	C(42)−N(3)−C(45)	104.8(10)
P(4)−Ru(2)	2.264(4)	C(60)−N(4)−C(63)	104.6(10)

Scheme 1



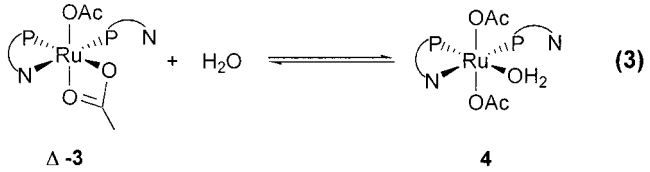
The $^{31}P\{^1H\}$ NMR spectrum of Δ-**3** in toluene exhibits two doublets with $J_{P-P} = 37$ Hz, which is typical for complexes with two nonequivalent *cis*-phosphine ligands. The lines remain sharp and do not split in the temperature interval 180−300 K, indicating that in solution the complex exists as a single epimer. Increasing the temperature above 300 K leads to gradual broadening and finally collapse of the signals at 370 ± 5 K. The

observed fluxional behavior can be explained in terms of the mechanism outlined in Scheme 1, with the calculated barrier of activation $\Delta G^{\ddagger} = 15.6 \pm 0.3$ kcal/mol.

Cross-peaks observed in the $^{31}P\{^1H\}$ ECSY NMR spectrum at 20 °C indicate that this process slowly occurs even at room temperature. No signals attributable to Λ-**3** or other products were detected in the $^{31}P\{^1H\}$ NMR spectra when Δ-**3** was kept for several days in a THF or toluene solution. It is conceivable therefore that the selective formation of Δ-**3** in the reaction 2 is thermodynamically controlled and Δ-**3** is more stable than the corresponding (Λ)-stereoisomer.

In comparison with complex **2**, which is rather inert, $[Ru(OAc)_2(PProMe)_2]$ readily reacts with water, undergoes facile isomerization in methanol, and smoothly transforms to carbene−ruthenium complexes upon thermolysis (see below).

Reaction of $[Ru(OAc)_2(PProMe)_2]$ with H_2O. X-ray Structure of $[Ru(OAc)_2(H_2O)(PProMe)_2]$. In solution complex Δ-**3** is extremely moisture sensitive and reacts readily with adventitious water, in accordance with eq 3.



(3)

Δ -3 4

It is common that ruthenium species containing chelating sulfonato[17] or acetato[18] ligands are very reactive with water to give the corresponding aqua complexes. There are also many examples of the Ru(II) aqua complexes stabilized by a combination of P and N donor ligands.[19]

Yellow crystalline **4**·C_5H_{10} (1:1 cyclopentane solvate) was isolated by recrystallization of Δ-**3**·C_5H_{10} from wet cyclopentane and characterized by elemental analysis, NMR spectroscopy, and single-crystal X-ray diffraction. An ORTEP plot of the complex is shown in Figure 3, while selected bond distances and angles are given in Table 3. The acetate ligands of **4** are monodentate and *trans* to each other. They lie essentially in plane with the aqua ligand. The short O(2)···O(5) and O(4)···O(5) interatomic separations (2.607 and 2.595 Å, respectively) suggest strong −C═O···HOH···O═C− hydrogen bonding. The mutual arrangement and coordination mode of the two aminophosphine ligands in **4** are exactly the same as those of complex Δ-**3**. The molecule of **4**, however, possesses only one bidentate ligand, and therefore the ruthenium is not stereogenic.

The $^{31}P\{^1H\}$ NMR spectrum of **4**·C_5H_{10} (dry THF, −40 °C) displays two intense doublets (46.5 and 55.8 ppm, $J_{P-P} = 37$ Hz) assigned to **4** along with two weak doublets (47.7 and 63.8 ppm, $J_{P-P} = 37$ Hz) belonging to Δ-**3**. The four doublets collapsed into two resonances, a broad doublet at 48 ppm ($J_{P-P} = 37$ Hz, $\Delta_{1/2} = 18$ Hz) and a broad signal centered at 58 ppm ($\Delta_{1/2} = 116$ Hz),

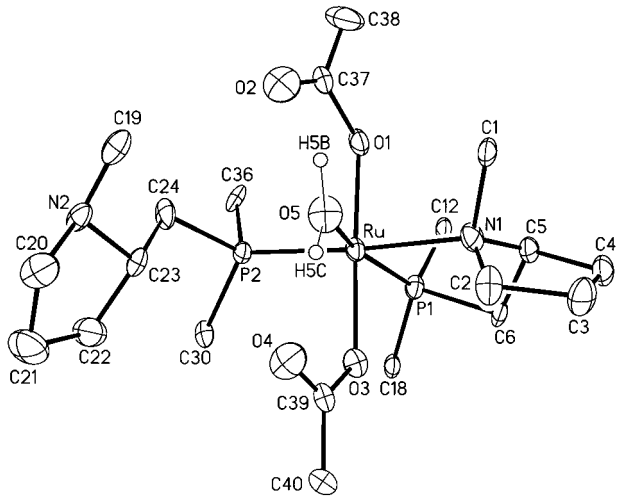


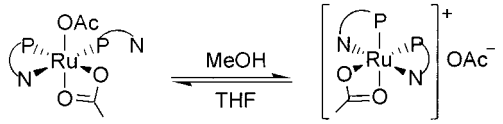
Figure 3. Perspective diagram of **4** with 30% probability ellipsoids. Hydrogen atoms (except for *O*-H) and non *ipso*-phenyl carbon atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 4·C_5H_{10}

O(1)−Ru	2.054(15)	N(1)−Ru	2.27(2)
O(3)−Ru	2.110(14)	P(1)−Ru	2.255(6)
O(5)−Ru	2.138(13)	P(2)−Ru	2.288(7)
C(1)−N(1)−C(2)	110.2(2)	C(1)−N(1)−Ru	109.9(13)
C(1)−N(1)−C(5)	102.9(17)	C(2)−N(1)−C(5)	108.5(18)

when the spectrum was recorded at 20 °C. Addition of excess water led to disappearance of the signals of Δ-**3** from the −40 °C spectrum and transformed the signals of **4** into two sharp doublets in the spectrum recorded at 20 °C. These data indicate that in solution complex **4** undergoes partial dissociation to Δ-**3** and water and the reaction 3 is indeed an equilibrium process ($K_{eq} \approx 1.5 \times 10^3$),[20] which is fast on the NMR time scale.

Isomerization of $[Ru(OAc)_2(PProMe)_2]$ in Methanol. X-ray Structure of $[Ru(OAc)(PProMe)_2]PF_6$. In methanol solution complex Δ-**3** undergoes spontaneous rearrangement to the cationic complex Λ-**5** (eq 4). The complete transformation takes ca. 1.5 h at room temperature and can be conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The signals of Δ-**3** gradually decrease in intensity, while the singlet at 55 ppm, assigned to Λ-**5**, simultaneously grows. The reaction 4 is reversible and complex Λ-**5** completely reverts back to Δ-**3** within 1.5 h when dissolved in THF or toluene.



(4)

Δ -3 Λ-5

The $^{31}P\{^1H\}$ NMR spectra of Λ-**5** in methanol recorded from −80 to 60 °C display a sharp singlet, indicating that in solution the complex exists as a single epimer. Attempts to obtain Λ-**5** in a crystalline form failed, so the complex was treated with $NaPF_6$ in methanol to afford the hexafluorophosphate salt (Λ-**6**), which precipitates from the solution as crystals suitable for X-ray analysis. Comparison of the NMR spectra of

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(18) Herold, S.; Mezzetti, A.; Venanzi, L. M.; Albinatti, A.; Lianza, F.; Gerfin, T.; Gramlich, V. *Inorg. Chim. Acta* **1995**, *235*, 215.

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(20) Calculated for 0.176 M solution of **4**·C_5H_{10} in THF at −40 °C.

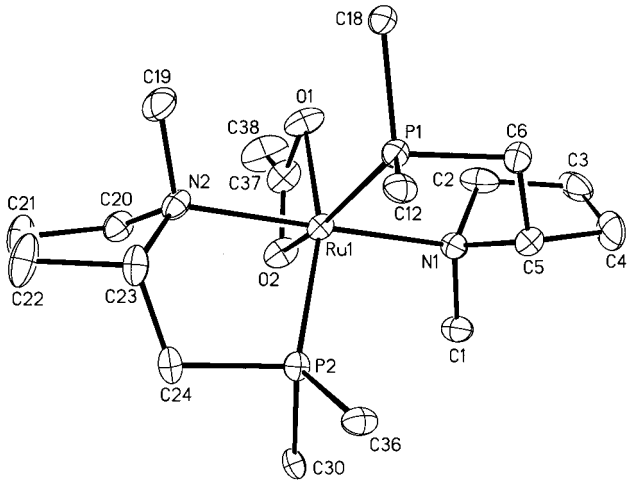


Figure 4. Perspective diagram of the complex cation of Λ-**6** with 30% probability ellipsoids. All hydrogen atoms and non *ipso*-phenyl carbon atoms are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Λ-6

O(1)−Ru(1)	2.213(5)	O(1)−Ru(1)−O(2)	59.84(17)
O(2)−Ru(1)	2.180(5)	P(1)−Ru(1)−P(2)	97.73(6)
N(1)−Ru(1)	2.191(5)	C(1)−N(1)−C(2)	106.0(5)
N(2)−Ru(1)	2.201(5)	C(1)−N(1)−C(5)	109.2(5)
P(1)−Ru(1)	2.2778(18)	C(1)−N(1)−Ru(1)	109.7(4)
P(2)−Ru(1)	2.2645(17)	C(2)−N(1)−C(5)	102.3(5)

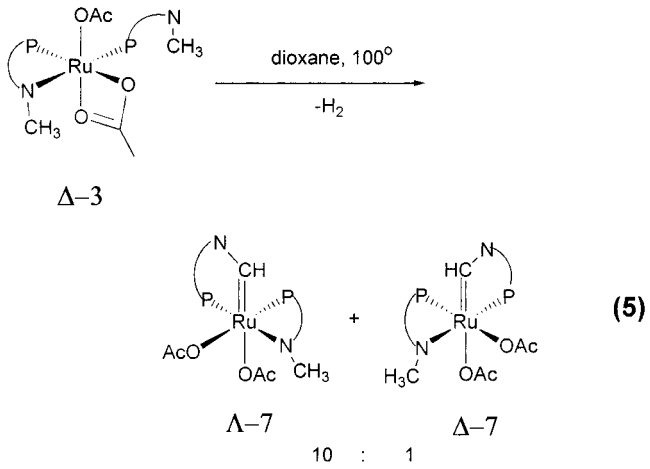
Λ-**5** and Λ-**6** (see Experimental Section) indicates that the structure of the complex cation is identical in both compounds.

The asymmetric unit of crystalline Λ-**6** consists of two octahedral Ru cations and two PF_6 anions. Although crystallographically distinct, the two cationic fragments are chemically indistinguishable (both are (Λ)-stereoisomers with the same spatial arrangement of atoms and have almost identical values for corresponding bond lengths and angles). An ORTEP plot showing an arbitrarily chosen complex cation of Λ-**6** is given in Figure 4. The selected bond distances and angles are presented in Table 4.

The octahedral coordination environment of ruthenium in Λ-**6** consists of a chelating acetato ligand and two *P,N*-chelating aminophosphines. The two P atoms are mutually *cis*, while the coordinated amino groups are *trans* to each other. Both [3.3.0] bicyclic systems of Λ-**6** are fused in the thermodynamically favorable *cis*-fashion; consequently both *N*-stereocenters of the complex adopt an *(S)*-configuration.

The detailed mechanism of the isomerization (eq 4) remains unclear, but perhaps it involves dissociation of one OAc ligand and rearrangement of the resulting pentacoordinate intermediate.

Formation of Ruthenium Carbene Complexes (Λ-7) and (Δ-7) upon Thermolysis of [Ru(OAc)$_2$-(PProMe)$_2$]. X-ray Structure of Δ-7. Refluxing Δ-**3** in dioxane or toluene solution leads to the evolution of hydrogen[21] and formation of the carbene complexes Λ-**7** and Δ-**7** in a 10:1 ratio (eq 5), along with ca. 10% of unidentified side products. According to the ^{31}P NMR spectra, the reaction is complete in 5 h.



(5)

In contrast to the (Λ)-diastereomer, Δ-**7** is only sparingly soluble in dioxane or toluene and precipitates upon concentration and cooling to room temperature. The complex was isolated as a yellow air-stable crystalline solid soluble in methanol or chlorinated hydrocarbons and characterized by elemental analysis and NMR spectroscopy. The solid state structure of Δ-**7** was established by a single-crystal X-ray diffraction study. An ORTEP plot of the complex is shown in Figure 5; the selected bond distances and angles are compiled in Table 5.

The octahedral coordination environment of the central Ru atom in Δ-**7** is formed by a *P,N*-chelating

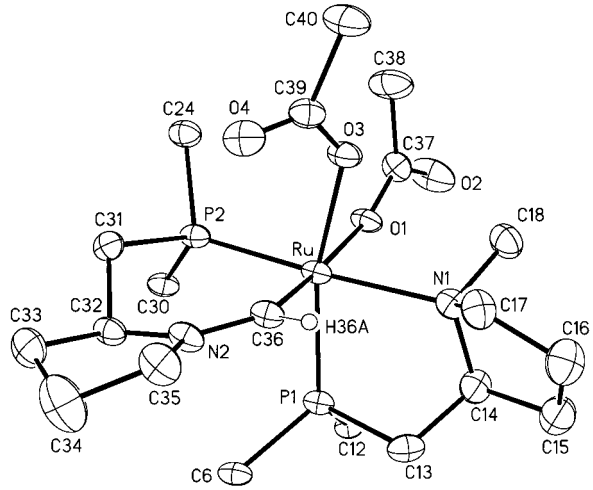


Figure 5. Perspective diagram of Δ-**7** with 30% probability ellipsoids. All hydrogen atoms (except for carbene-H) and non *ipso*-phenyl carbon atoms are omitted for clarity.

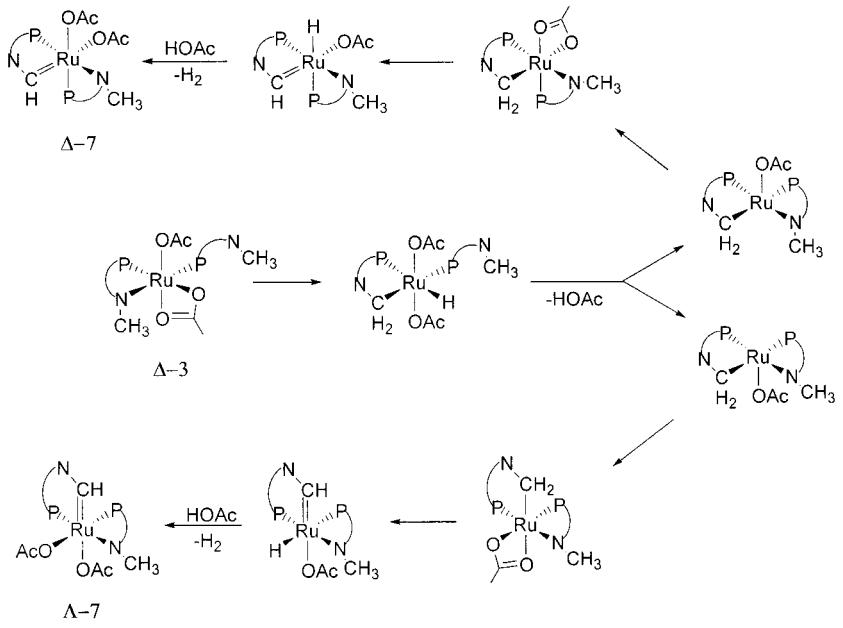
Table 5. Selected Bond Distances (Å) and Angles (deg) for Δ-7·C$_6$H$_6$

Ru−C(36)	1.939(3)	C(36)−N(2)	1.324(4)
Ru−N(1)	2.313(3)	C(18)−N(1)	1.492(5)
Ru−O(1)	2.220(3)	C(32)−N(2)	1.476(5)
Ru−O(3)	2.117(2)	C(35)−N(2)	1.489(4)
Ru−P(1)	2.2915(9)	C(14)−N(1)	1.488(5)
Ru−P(2)	2.2427(11)	C(17)−N(1)	1.505(5)
C(36)−Ru−N(1)	93.23(13)	C(32)−N(2)−C(35)	111.7(3)
C(36)−Ru−O(3)	90.76(12)	N(2)−C(36)−Ru	134.3(3)
C(36)−Ru−P(1)	87.35(10)	C(14)−N(1)−Ru	112.5(2)
C(36)−Ru−P(2)	90.75(11)	C(17)−N(1)−Ru	117.0(2)
N(1)−Ru−P(1)	81.70(8)	C(18)−N(1)−Ru	109.2(3)
P(1)−Ru−P(2)	100.16(4)	C(14)−N(1)−C(17)	102.9(3)
C(36)−N(2)−C(32)	127.4(3)	C(14)−N(1)−C(18)	108.3(3)
C(36)−N(2)−C(35)	120.5(3)	C(17)−N(1)−C(18)	106.5(3)

(21) Formation of ca. 1 equiv H_2 was confirmed by collecting the released gas and GC analysis.

(22) See for example: Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1998**, *17*, 827, and references therein.

Scheme 2



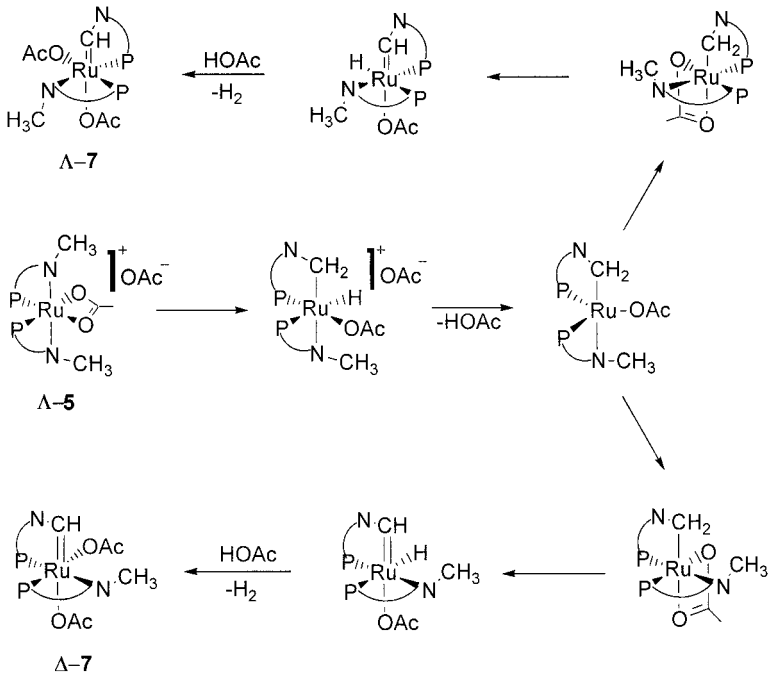
aminophosphine, the phosphine-carbene chelate, and two mutually *cis* monodentate OAc ligands. The coordinated amino group is *trans* to one of the two phosphorus atoms, which in turn are *cis* to each other and to the carbene moiety. The C(32)−C(35)−N(2)−C(36)−Ru fragment is essentially planar, which indicates a high degree of conjugation in the Ru−carbene−nitrogen system. Thus, the carbene−nitrogen bond (1.324 Å) is significantly shorter than the corresponding methyl−nitrogen bond (1.492 Å) in the *P,N*-chelating aminophosphine. The ruthenium−carbene carbon distance is comparable to those of other Fisher type carbene−Ru complexes reported in the literature.[22] As expected, the [3.3.0] bicyclic system of Δ-**7** adopts the thermodynamically more stable *cis*-fused configuration and the stereogenic nitrogen of the *P,N*-chelate is of *(S)*-absolute configuration.

The main product of the reaction 5, complex Λ-**7**, was isolated as an air-stable yellow-orange solid, soluble in common organic solvents except for saturated hydrocarbons. Attempts to obtain Λ-**7** in crystalline form were unsuccessful; however, its composition and stereochemistry were deduced from NMR data. Comparison of the NMR spectra of Λ-**7** with those of the (Δ)-diastereomer indicates that these complexes possess similar structures. Both compounds display a pair of doublets in their $^{31}P\{^1H\}$ NMR spectra at 50.4 and 55.8 ppm ($J_{P-P} = 32$ Hz) for Δ-**7**, and at 45.4 and 64.5 ppm ($J_{P-P} = 32$ Hz) for Λ-**7**, due to nonequivalent *cis*-phosphines. The values of the J_{C-P} coupling constants for low-field triplets observed in the $^{13}C\{^1H\}$ NMR spectra at 242.5 ppm ($J_{C-P1} \approx J_{C-P2} = 15$ Hz) for Δ-**7** and at 242.8 ppm ($J_{C-P1} \approx J_{C-P2} = 15$ Hz) for Λ-**7** indicate that the carbene ligand is *cis* to both P atoms in both complexes. Other carbons of Λ-**7** give ^{13}C NMR signals with chemical shift values close to those for the corresponding carbons of Δ-**7** (see Experimental Section). The coordinated amino group of Λ-**7** gives a doublet in the $^{15}N\{^1H\}$ NMR spectrum at δ −320.4 ($J_{N-P} = 32$ Hz). The value of the coupling constant[23] is indicative of a *trans* relationship between the nitrogen and one of the two phosphorus atoms (the *cis* N−P coupling constants are often smaller than 1 Hz and therefore not observed). Taken together these data suggest that the two complexes relate to each other as a pair of epimers. Since the configurations of the corresponding stereocenters at nitrogen and carbon atoms are the same in both compounds and one of them is the structurally characterized (Δ)-stereoisomer, the other complex should possess (Λ)-configuration.

According to ^{31}P NMR no (Δ−Λ) or (Λ−Δ) interconversion occurred when the isolated Δ-**7** or Λ-**7** was kept in methanol or dioxane solution for 1 week at room temperature. However, when heated in sealed NMR tubes immersed in an oil bath (t_{bath} 130 °C) as dioxane solutions, both complexes underwent fast epimerization affording ca. 1:8 mixture of (Δ)- and (Λ)-stereoisomers. This ratio was attained in 2 h and then remained constant under prolonged (up to 24 h) heating. In boiling dioxane (bp 101 °C) the epimerization is sluggish. When isolated Δ-**7** is heated under these conditions, ca. 20:1, 8:1, 3:1, and 1:1 Δ/Λ ratios were observed after 3, 5, 12, and 24 h, respectively. These data show that Λ-**7** is thermodynamically more stable than the corresponding (Δ)-stereoisomer. The preferential formation of Λ-**7** however is kinetically controlled and cannot be explained by simultaneous epimerization, since it occurs significantly slower than the thermolysis of Δ-**3**. The possible mechanism for reaction 5 may involve *β*-H abstraction from the coordinated amino group of Δ-**3** followed by reductive elimination of HOAc (Scheme 2). The subsequent α-H abstraction from the resulting alkyl-ruthenium intermediates may lead either to Δ-**7**

(23) The values of *cis* P−N and *trans* P−N constants in metallocomplexes normally lie within 0−6 Hz and 25−95 Hz, respectively. See for example: (a) Kuznetsov, V. F. Facey, G. A.; Yap, G. P. A.; Alper, H. *Organometallics* **1999**, *18*, 4706. (b) Carlton, L. Weber, R. *Inorg. Chem*. **1996**, *35*, 5843. (c) Heaton, B. T.; Jacob, C.; Monks, G. L.; Hursthouse M. B.; Ghatak, I.; Somervile R. G.; Heggie, W.; Page, P. R.; Villax, I. *J. Chem. Soc., Dalton Trans*. **1996**, 61. (d) Carlton, L. De Sousa, G. *Polyhedron*, **1993**, *12*, 1377.

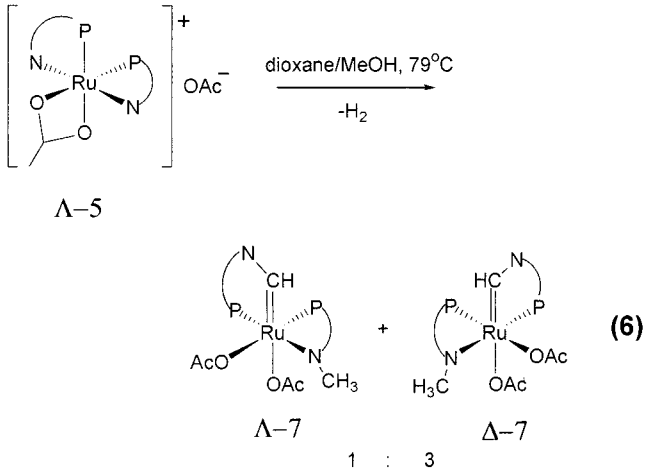
Scheme 3



or to Λ-**7** depending on which of the two acetate ligands remains coordinated.

A similar sequence of β-H and α-H elimination from the coordinated NMe_2 fragment leading to the formation of a carbene tantalum complex has been reported,[24] and intramolecular C−H bond activation of the *N*-Me group in Ru complexes is a well-documented process.[25,26] It should be noted, however, that mechanisms other than that proposed in Scheme 2 are possible. For example, oxidative addition of the C−H bond is not strictly necessary. An alternative pathway may include deprotonation of the coordinated *N*-Me group by an acetate ligand. Moreover, the uncoordinated amino group may also react via agostic C−H bonding after the OAc ligand has vacated a coordination site by changing from chelating to monodentate. We cannot rule out any of these possibilities. However, the latter appears to be less probable, as the thermolysis of Λ-**5**, which possesses no pendant amino groups, occurs significantly faster than that of Δ-**3** (see below).

Thermolysis of Δ-**3** in a 6:1 dioxane−methanol solution affords thermodynamically less stable Δ-**7** as the major product. The reaction is complete in 3 h to give Δ-**7** and Λ-**7** in approximately 3:1 ratio, along with ca. 10% of unidentified products. Such reversed selectivity is not the result of the lower reaction temperature. Indeed thermolysis of Δ-**3** in a 2:1 dioxane−THF solution, which has the same boiling point (79 °C) as the 6:1 dioxane−methanol mixture, proceeded significantly slower (ca. 10 h for complete conversion) and led to formation of Δ-**7** and Λ-**7** in the same 1:10 ratio as was observed for thermolysis in neat dioxane. The ^{31}P NMR monitoring of the reaction in dioxane−methanol shows that on refluxing for 10 min the signals of Δ-**3** completely disappeared from the spectra. At this point the spectra displayed an intense singlet at 55 ppm assigned to complex Λ-**5** (see eq 4) along with weak signals of Δ-**7** and Λ-**7**. Further heating led to gradual disappearance of the singlet accompanied by increase of the signals due to Δ-**7** and Λ-**7**. These data suggest that under the reaction conditions Δ-**3** is initially transformed into the cationic species Λ-**5**, which then undergoes thermolysis in accordance with eq 6.



(6)

Analogous to reaction 5, several mechanisms can be proposed for the thermolysis of Λ-**5**. One of the possible mechanisms is shown in Scheme 3 and includes key steps similar to those suggested for reaction 5. The pentacoordinate intermediate can be formed via C−H oxidative addition/HOAc reductive elimination, as is shown in Scheme 3, or alternatively, by deprotonation of the NMe group by the OAc ligand or OAc anion. The preferential formation of Δ-**7** is kinetically controlled. Perhaps the rearrangement of the pentacoordinate intermediate leading to the formation of Δ-**7** has a lower

(24) de Castro, I.; Galakhov, M. V.; Gómez, M.; Gómez-Sal, P.; Royo, P. *Organometallics* **1996**, *15*, 1362.
(25) Mauthner, K.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 1956.
(26) Steenwinkel, P.; James, S. L.; Gossage, R. A.; Grove, D. M.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *117*, 4680, and references therein.

activation barrier than that of a Berry pseudorotation or turnstile rotation[27] leading to Λ-**7**.

Conclusions

Ruthenium complexes of general formula $[Ru(OAc)_2(P,N)_2]$ can be readily prepared from ruthenium acetate and aminophosphines **1a**,**b**. The balance of electronic and steric factors, which defines the structure of these complexes, is very delicate and easily affected by solvation or intramolecular hydrogen bonding. Thus $[Ru(OAc)_2(PPro)_2]$ displays *trans-P,P*, *trans-N,N* coordination geometry, whereas $[Ru(OAc)_2(PProMe)_2]$ exists as the *cis-P,P*, *cis-P,N* (Δ)-stereoisomer in THF and as the (Λ)-stereoisomer with a *cis-P,P*, *trans-N,N* configuration in methanol. The selective formation of *N*-based stereocenters in $[Ru(OAc)_2(PProMe)_2]$ is explained by the higher thermodynamic stability of *cis* (as compared to *trans*) fused [3.3.0] bicyclic systems arising upon chelation to Ru. The relative stability of *cis*- and *trans*-fused ring systems is not important in the case of $[Ru(OAc)_2(PPro)_2]$, where hydrogen bonding renders *N*-H protons on the opposite sides of the P−N−N−P equatorial plane of the molecule and thus defines the absolute configuration of the *N*-stereocenters.

Experimental Section

All manipulations were carried out under inert atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use. Anhydrous lithium acetate was prepared by heating $LiOAc{\cdot}2H_2O$ in a vacuum at 100−120 °C for 2 h; a glass filter was used to prevent the dust from entering the vacuum line. Aminophosphines **PPro**[10] and **PProMe**[11] were prepared by slight modifications of the published procedures. Other chemicals were purchased from Strem or Aldrich and used as received. The following instruments were used: Varian XL-300 and Bruker AMX 500 (NMR) and Perkin-Elmer 2400 Series II (combustion microanalysis). The natural abundance $^{15}N\{^1H\}$ NMR spectrum of Λ-**7** was acquired using a 0.9 M solution of the complex in a 1:10 $C_6D_6-C_6H_6$ mixture, 10 mm probe, CH_3NO_2 as external standard, D1 = 12 s, gated decoupling. The spectrum with acceptable (10:1) signal-to-noise ratio was observed after 18 h.

Synthesis of $[Ru_2(OAc)_4]{\cdot}2THF$. Method A. Ruthenium(III) chloride hydrate (41.6% Ru, 600 mg, 2.47 mmol), lithium acetate (1.2 g, 18.2 mmol), and platinum on carbon (10% Pt, 30 mg) were placed in a 100 mL glass autoclave, which was purged with nitrogen and charged with methanol (16 mL), acetic anhydride (1 mL), and hydrogen (4 atm). The reaction mixture was stirred for 2 h at ambient temperature and 0.5 h at 120−130 ° C (t_{bath}) and then allowed to cool to room temperature The formed brown precipitate was separated by filtration, washed with methanol (4 × 10 mL), dried in a vacuum, and dissolved in hot THF (10 mL). The brown solution was filtered, the residue was washed with THF (5 mL), and the combined filtrates were taken to dryness under vacuum at room temperature to give $[Ru_2(OAc)_4]{\cdot}2THF$ (583 mg, 1.0 mmol, 81%) as black-brown shining crystals. Anal. Calcd for $C_{16}H_{28}O_{10}Ru_2$: C, 32.99; H, 4.85. Found: C, 32.69; H, 4.74.

Method B. Hydrogen was slowly bubbled through a stirred mixture of ruthenium(III) chloride hydrate (41.21% Ru, 600 mg, 2.45 mmol), LiOAc (1.2 g, 18.2 mmol), platinum on carbon (10% Pt, 30 mg), MeOH (16 mL), and acetic anhydride (1 mL) while the mixture was heated to reflux. After 4 h the reaction mixture was cooled to room temperature, and $[Ru_2(OAc)_4]{\cdot}2THF$ (418 mg, 0.72 mmol, 58%) was isolated in the same way as described for method A.

Synthesis of $[Ru(OAc)_2(PPro)_2]{\cdot}MeOH$. PPro (1.245 mmol, 0.344 M in toluene) was added to a suspension of $[Ru_2(OAc)_4]{\cdot}2THF$ (164 mg, 0.281 mmol) in methanol (10 mL). The mixture was stirred for 15 min, the resulting clear yellow solution was evaporated under vacuum, and the residue was dissolved in CH_2Cl_2 (5 mL). The resulting solution was diluted with MeOH (10 mL), reduced in volume to ca. 8 mL under vacuum, and left overnight at room temperature The precipitated crystalline yellow solid was separated by decantation, washed with methanol (2 × 3 mL), and dried in a vacuum to give 298 mg of analytically pure $Ru(OAc)_2(Ph_2PPro)_2{\cdot}MeOH$. An additional 48 mg of the complex was isolated upon concentration of the mother liquor. The total yield was 346 mg (0.438 mmol, 78%). Anal. Calcd for $C_{39}H_{50}N_2O_5P_2Ru$: C, 59.31; H, 6.38; N, 3.55. Found: C, 59.12; H, 6.52; N, 3.48. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.9 (d, J = 334 Hz); 45.6 (d, J = 334 Hz). ^1H NMR ($CDCl_3$): δ 0.9 (s, 3H); 1.4−1.9 (m, 4H); 1.6 (s, 3H); 2.1 (m, 4H); 2.3−3.1 (m, 9H); 3.3 (s, 3H, MeOH), 3.7 (m, 1H); 7.2−7.6 (m, 20H); 8.5 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.4 (s, CH_3); 24.9 (s, CH_2); 25.8 (s, CH_3); 27.5 (s, CH_2); 30.2 (d, J_{C-P} = 15 Hz, CH_2); 31.9 (d, J_{C-P} = 13 Hz, CH_2); 32.2 (d, J_{C-P} = 16 Hz, CH_2); 38.2 (d, J_{C-P} = 21 Hz, CH_2); 50.3 (s, MeOH); 52.1 (s, CH_2); 52.3 (s, CH_2); 61.2 (m, CH); 64.9 (m, CH); 127.8−129.2 (18 lines, Ph); 132.3−137.4 (31 line, Ph); 182.7 (s, OAc); 184.5 (s, OAc).

Synthesis of $[Ru(OAc)_2(PProMe)_2]{\cdot}C_5H_{10}$. PProMe (0.950 mmol, 0.465 M in toluene) was added to a stirred solution of $[Ru_2(OAc)_4]{\cdot}2THF$ (138 mg, 0.237 mmol) in THF (8 mL). The mixture was stirred for 15 min, and the resulting clear orange solution was evaporated under vacuum. The residue was dissolved in cyclopentane (8 mL), and the solution was filtered and kept at room temperature until a dark orange crystalline mass precipitated.[28] The crystals were separated by decantation, washed with cyclopentane (2 × 3 mL), and dried in a vacuum to give 297 mg of analytically pure $[Ru(OAc)_2(PProMe)_2]{\cdot}C_5H_{10}$. An additional 45 mg of the complex was isolated upon concentration of mother liquor. The total yield was 342 mg, 0.399 mmol, 84%. Anal. Calcd for $C_{45}H_{60}N_2O_4P_2Ru$: C, 63.14; H, 7.06; N, 3.27. Found: C, 63.15; H, 7.14; N, 3.26. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 48.9 (d, J = 37 Hz); 63 (d, J = 37 Hz). ^1H NMR ($CDCl_3$): δ 0.6 (m, 1H); 0.9 (m, 1H); 1.1−2.0 (m, 10H); 1.2 (s, 3H); 1.3 (m, 10H, C_5H_{10}); 1.7 (s, 3H); 1.9 (s, 3H); 2.1(s, 3H); 2.3 (m, 1H); 2.5−3.0 (m, 4H); 3.4 (m, 1H); 6.9−7.4 (m, 20H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.1 (s, Me); 23.5 (s, CH_2); 23.9 (s, Me); 25.1 (s, CH_2); 25.4 (s, C_5H_{10}); 28.0 (d, J_{C-P} = 13 Hz, CH_2); 29.0 (d, J_{C-P} = 21 Hz, CH_2); 31.2 (s, CH_2); 39.8 (s, Me); 40.3 (d, J_{C-P} = 27 Hz, CH_2); 47.8 (s, Me); 56.0 (s, CH_2); 56.7 (s, CH_2); 61.5 (d, J_{C-P} = 7.5 Hz, CH); 68.1 (s, CH); 126.4−136.8 (Ph); 180.0 (s, OAc); 186.2 (s, OAc). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 55.0 (s). ^1H NMR (CD_3OD): δ 1.3 (m, 10H, C_5H_{10}); 1.7−2.0 (m, 8H); 1.9 (s, 3H); 2.2 (m, 2H); 2.3 (s, 3H); 2.5 (s, 6H); 2.7 (m, 2H); 2.9 (m, 2H); 3.2−3.5 (m, 4H); 7.0 (m, 4H); 7.2 (t, J = 7.5 Hz, 4H); 7.3−7.4 (m, 8H); 7.7 (m, 4H).$^{13}C\{^1H\}$ NMR (CD_3OD): δ 20.1 (s, CH_2); 24.5 (s, CH_3); 25.3 (s, CH_3); 25.6 (s, C_5H_{10}); 26.8 (vt, J_{C-P} = 13 Hz, CH_2); 42.3 (m, CH_2); 54.2 (s, CH_3); 59.5 (s, CH_2); 74.4 (s, CH); 129.5 (vt, J_{C-P} = 10 Hz, Ph);130.3 (vt, J_{C-P} = 9 Hz, Ph); 130.5 (s, Ph); 130.7 (s, Ph); 132.1 (vt, J_{C-P} = 8 Hz, Ph); 133.6 (vt, J_{C-P} = 9 Hz, Ph); 133.7 (vt, J_{C-P} = 43 Hz, Ph); 140.6 (second-order m, Ph); 179.6 (s, OAc); 192.0 (t, J_{C-P} = 2.5 Hz, OAc). $^{15}N\{^1H\}$ NMR (CD_3OD: CH_3OH = 1:10): δ −345.1 (s).

Synthesis of $[Ru(OAc)(PProMe)_2]PF_6$. PProMe (1.98 mmol, 0.465 M in toluene) was added to a stirred suspension of $[Ru_2(OAc)_4]{\cdot}2THF$ (286 mg, 0.572 mmol) in MeOH (10 mL). The resulting orange solution was treated with solid $NaPF_6$ (200 mg, 1.19 mmol), stirred for 15 min, filtered through cotton

(27) Ugi, I.; Marquarding, D.; Klusacek, H.; Gillespie, P. *Acc. Chem. Res.* **1971**, *4*, 288.

(28) Addition of seed crystals leads to complete crystallization within 3 h, otherwise it may take several days.

Table 6. Summary of Crystallographic Data for 2·Et_2O, Δ-3·C_5H_{10}, 4·C_5H_{10}, Λ-6, and Δ-7·C_6H_6

	2·Et_2O	Δ-**3**·C_5H_{10}	**4**·C_5H_{10}	Λ-**6**	Δ-**7**·C_6H_6
formula	$C_{42}H_{56}N_2O_5P_2Ru$	$C_{45}H_{60}N_2O_4P_2Ru$	$C_{45}H_{62}N_2O_5P_2Ru$	$C_{38}H_{47}F_6N_2O_2P_3Ru$	$C_{46}H_{54}N_2O_4P_2Ru$
fw	831.90	855.96	873.97	871.76	861.92
cryst dimens, mm	0.2 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.3 × 0.3 × 0.1	0.1 × 0.1 × 0.2	0.3 × 0.2 × 0.2
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
a, Å	15.373(1)	10.216(3)	9.790(5)	9.9950(7)	15.431(2)
b, Å	15.911(1)	21.508(6)	20.021(9)	39.365(3)	16.229(2)
c, Å	16.641(1)	19.816(5)	12.838(9)	10.0685(7)	17.424(2)
β, deg	108.044(1)	98.556(3)	101.32(1)	98.6570(10)	90
space group	C_2	$P2_1$	$P2_1$	$P2_1$	$P2_12_12_1$
Z	4	4	2	4	4
V, Å^3	3870.1(5)	4306(2)	2467(2)	3916.3(5)	4363.2(7)
d_{calc}, g/cm^3	1.428	1.329	1.178	1.479	1.312
T, K	203(2)	293(2)	203(2)	203(2)	203(2)
radiation (*λ*)			Mo Kα (0.71073 Å)		
abs coeff, mm^{-1}	0.535	0.482	0.423	0.587	0.476
transmissn (max/min)	1.33580	1.59535	1.33198	1.39534	1.33187
R(*F*),%	4.33	5.68	8.60	6.09	4.12
R(*wF*^{2}),%	10.06	12.34	22.38	12.60	9.47
GOF	1.070	1.040	1.043	1.009	1.002
Flack param	−0.01(4)	0.05(5)	−0.05	−0.01(3)	−0.04

[a] Quantity minimized = $R(wF^2) = \sum[(w(F_o^2 - F_c^2)^2]/\sum(wF_o^2)^{1/2}$; $R(F) = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$.

wool, reduced in volume to ca. 5 mL, and allowed to stay at 5 °C for 2 h. The formed orange crystalline solid was separated by decantation, rinsed with cold MeOH (3 mL), and dried in a vacuum to give analytically pure [Ru(OAc)(PProMe)$_2$]PF_6 (499 mg, 0.572 mmol, 58%). Anal. Calcd for $C_{38}H_{47}F_6N_2O_2P_3Ru$: C, 52.35; H, 5.43; N, 3.21. Found: C, 52.26; H, 5.28; N, 3.12. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −143.8 (sept, J_{P-F} = 713 Hz); 51.6 (s). ^1H NMR (CD_2Cl_2): δ 1.8−2.3 (m, 10H); 2.4 (s, 3H); 2.6 (s, 6H); 2.7 (m, 2H); 2.9 (m, 2H); 3.1 (m, 2H); 3.4 (m, 2H); 6.9 (m, 4H); 7.1 (t, *J* = 7.5 Hz, 4H); 7.3 (m, 8H); 7.6 (m, 4H).$^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 19.3 (s, CH_2); 25.2 (s, CH_3); 26.1 (vt, J_{C-P} = 13 Hz, CH_2); 43.3 (m, CH_2); 56.4 (s, CH_3); 57.3 (s, CH_2); 73.2 (s, CH); 128.6 (vt, J_{C-P} = 10 Hz, Ph);129.2 (vt, J_{C-P} = 9 Hz, Ph); 129.4 (s, Ph); 129.8 (s, Ph); 130.5 (vt, J_{C-P} = 7 Hz, Ph); 132.4 (vt, J_{C-P} = 8 Hz, Ph); 138.9 (vt, J_{C-P} = 44 Hz, Ph); 139.4 (vt, J_{C-P} = 44 Hz, Ph); 190.1 (t, J_{C-P} = 2.5 Hz, OAc).

Synthesis of [Ru(OAc)$_2$(H$_2$O)(Ph$_2$PProMe)$_2$]·C_5H_{10}. Water (50 μL, 2.77 mmol) was added to a stirred solution of Δ-**3**·C_5H_{10} (1.29 g, 1.51 mmol) in warm cyclopentane (15 mL), causing an immediate color change from orange to light yellow. The resulting solution was reduced in volume to ca. 8 mL under vacuum and left overnight. The precipitated yellow crystals were separated by decantation, washed with C_5H_{10}, and dried in a vacuum to give 735 mg of analytically pure **4**·C_5H_{10}; an additional 446 mg was isolated upon concentration of the mother liquor. The total yield of **4**·C_5H_{10} was 1.18 g (1.35 mmol, 89%). Anal. Calcd for $C_{45}H_{62}N_2O_5P_2Ru$: C, 61.84; H, 7.15; N, 3.21. Found: C, 61.53; H, 7.28; N, 3.12. $^{31}P\{^1H\}$ NMR (toluene-d_8, −40 °C): δ 49.5 (d, *J* = 37 Hz); 58.4 (d, *J* = 37 Hz). ^1H NMR (toluene-d_8, −40 °C): δ 0.9 (m, 2H); 1.2 (m, 2H); 1.4−1.9 (m, 5H); 1.6 (s, 10H); 1.8 (s, 3H); 2.1 (s, 3H); 2.3 (m, 2H); 2.4 (s, 3H); 2.5 (s, 3H); 2.6−3.1 (m, 5H); 3.4 (m, 1H); 3.6 (m, 1H); 5.3 (b.s, 2H); 7.0−7.4 (m, 16H); 7.8 (m, 4H). $^{13}C\{^1H\}$ NMR (toluene-d_8, −40 °C): δ 22.2 (s, CH_2); 22.4 (s, CH_2); 25.4 (s, CH_3); 26.0 (s, CH_3); 26.2 (s, C_5H_{10}); 28.01 (d, J_{C-P} = 13 Hz, CH_2); 32.6 (s, CH_2); 33.7 (d, J_{C-P} = 19 Hz, CH_2); 40.3 (s, CH_3); 41.8 (d, J_{C-P} = 27 Hz, CH_2); 46.1 (s, CH_3); 54.9 (s, CH_2); 56.1 (s, CH_2); 62.3 (d, J_{C-P} = 7 Hz, CH); 68.4 (d, J_{C-P} = 5 Hz, CH); 127.4−129.8 (Ph); 133.6−138.1 (Ph); 183.2 (s, OAc); 183.4 (s, OAc).

Synthesis of Δ-7. Method A. A stirred solution of [Ru(OAc)$_2$(ProMe)$_2$]·C_5H_{10} (3.14 g, 3.66 mmol) in a mixture of dioxane (18 mL) and MeOH (3 mL) was heated to reflux for 3 h, reduced in volume to ca. 16 mL, and cooled to room temperature. The formed voluminous precipitate was separated by filtration, washed with benzene (2 × 4 mL), and dried in a vacuum to give 1.18 g of analytically pure Δ-**7**. An additional 223 mg was isolated upon concentration of the mother liquor. The total yield of Δ-**7** was 1.40 g, 1.79 mmol, 49%. Anal. Calcd for $C_{40}H_{48}N_2O_4P_2Ru$: C, 61.21; H, 6.17; N, 3.57. Found: C, 61.29; H, 6.23; N, 3.40. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 50.4 (d, *J* = 32 Hz); 55.8 (d, *J* = 32 Hz). ^1H NMR ($CDCl_3$): δ 1.0 (s, 3H); 1.4−2.2 (m, 9H); 1.9 (s, 3H); 2.4 (s, 3 H); 2.6 (m, 2H); 3.0 (m, 2H); 3.7 (m, 1H); 4.3 (m, 1H); 4.9 (m, 1H); 6.3 (m, 2H); 6.8−7.7 (m, 20H); 12.4 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.6 (s, CH_3); 23.4 (s, CH_2); 23.5 (s, CH_2); 25.1 (s, CH_2); 26.5 (d, J_{C-P} = 14 Hz, CH_2); 31.9 (d, J_{C-P} = 32 Hz, CH_2); 34.8 (d, J_{C-P} = 13 Hz, CH_2); 43.0 (d, J_{C-P} = 34 Hz, CH_2); 47.0 (s, CH_3); 57.2 (s, CH_2); 57.8 (s, CH); 60.8 (s, CH_2); 66.3 (s, CH); 127.2−133.4 (Ph); 175.8 (s, OAc); 186.5 (s, OAc); 242.5 (t, J_{C-P} = 15 Hz, CH).

Method B. A stirred solution of [Ru(OAc)$_2$(ProMe)$_2$]·C_5H_{10} (2.12 g, 2.48 mmol) in dioxane (20 mL) was heated to reflux for 6 h and then evaporated to dryness. The residue was dissolved in benzene (10 mL), and the resulting orange-brown solution was set aside for 2 h. The formed voluminous precipitate was separated by filtration, washed with benzene (2 × 2 mL), and dried in a vacuum to give 146 mg of Δ-**7**. The combined washings and filtrate were diluted with heptane (10 mL) and reduced in volume to ca. 10 mL under vacuum to give an orange solution and brown oily residue. The solution was discarded, and the residue was washed with heptane (2 × 10 mL) and dissolved in benzene. The resulting solution was left at room temperature overnight. The formed yellow crystals were separated by filtration, washed with benzene (2 × 2 mL), and dried in a vacuum to give an additional 32 mg of Δ-**7**. The total yield was 178 mg, 0.227 mmol, 9%.

Synthesis of Λ-7. The supernatant and washings collected after the separation of complex Δ-**7** by method B (see above) were evaporated to dryness under vacuum. The residue was stirred with cyclopentane (10 mL) to give a yellow solid and yellow solution. The solid was separated by decantation and dried in a vacuum to give 1.43 g of crude Λ-**7**. The complex was ca. 90% pure (^{31}P NMR) and contained a nonstoichiometric amount of benzene (^{13}C and ^1H NMR). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 45.4 (d, *J* = 32 Hz); 54.5 (d, *J* = 32 Hz). ^1H NMR (C_6D_6): δ 0.7 (m, 2H); 1.1 (m, 3H); 1.3−1.6 (m, 4H); 1.5 (s, 3H); 1.8 (m, 1H); 2.2 (m, 1H); 2.3 (s, 3H); 2.6 (m, 1H); 3.0 (s, 3H); 3.2 (m, 1H); 3.5 (m, 2H); 4.4 (m, 2H); 5.4 (m, 1H); 6.9−7.7 (m, 20H); 12.8 (s,1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 21.1 (s, CH_2); 22.1 (s, CH_2); 24.4 (s, CH_3); 24.5 (s, CH_3); 27.9 (d, J_{C-P} = 11 Hz, CH_2); 28.8 (d, J_{C-P} = 31 Hz, CH_2); 35.0 (d, J_{C-P} = 12 Hz, CH_2); 44.0 (d, J_{C-P} = 29 Hz, CH_2); 45.8 (s, CH_3); 58.6 (s, CH_2); 59.5 (s, CH); 60.7 (s, CH_2); 68.4 (s, CH); 128.2−136.7 (Ph); 175.1 (s, OAc);

185.9 (d, $J_{C-P} = 2$ Hz, OAc); 242.8 (t, $J_{C-P} = 15$ Hz, CH). $^{15}N\{^1H\}$ NMR (C_6D_6:C_6H_6 = 1:10): δ −320.4 (d $J_{N-P} = 32.6$ Hz); −165.8 (s).

Single-Crystal X-ray Diffraction Study of 2·Et$_2$O, Δ-3·C$_5$H$_{10}$, 4·C$_5$H$_{10}$, Λ-6, and Δ-7·C$_6$H$_6$. Crystals of **2**·Et_2O, suitable for X-ray analysis, were obtained by slow diffusion of ether into a CH_2Cl_2 solution of **2**·MeOH. Single crystals of Δ-**3**·C_5H_{10}, **4**·C_5H_{10} Λ-**6**, and Δ-**7**·C_6H_6 were obtained by slow crystallization of the corresponding complexes from concentrated solutions in C_5H_{10}, wet C_5H_{10}, MeOH, and C_6H_6, respectively. Compound **4**·C_5H_{10} consistently crystallized as thin stacked plates, and the reported diffraction data represent the best result of several attempts. The crystals were mounted on thin glass fibers using viscous oil and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0°, 90°, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[29] Systematic absences in the diffraction data and unit-cell parameters were consistent for space groups $P2_1$ and $P2_1/m$ for Δ-**3**·C_5H_{10}, Λ-**6**, and **4**·C_5H_{10}; C_2, C_m, and $C2/m$ for **2**·Et_2O; and, uniquely, $P2_12_12_1$ for Δ-**7**·C_6H_6. Solutions in the acentric space groups are consistent with the enantiomerically pure compounds. Only the space group C_2 yielded chemically reasonable and computationally stable results of refinement for **2**·Et_2O. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. An inspection of the resulting packing diagrams did not suggest any overlooked symmetry. Refinement of the Flack parameter in each case yielded nil, indicating that the true hands of the data sets have been determined. Two symmetry-unique compound molecules were located in the asymmetric unit of Δ-**3**·C_5H_{10} and Λ-**6**. Two molecules of cyclopentane, two half-molecules of diethyl ether, a cyclopentane molecule, and two half-occupied molecules of benzene, treated as idealized, rigid, flat hexagons, were located in the asymmetric units of Δ-**3**·C_5H_{10}, **2**·Et_2O, **4**·C_5H_{10}, and Δ-**7**·C_6H_6, respectively. The benzene and cyclopentane carbon atoms were refined isotropically. All other non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHEXTL 5.10 program library.[30]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for support of this research.

Supporting Information Available: Listing of crystallographic details, atomic parameters, bond distances and angles, and isotropic and anisotropic thermal parameters and ORTEP drawings for **2**·Et_2O, Δ-**3**·C_5H_{10}, **4**·C_5H_{10}, Λ-**6**, and Δ-**7**·C_6H_6. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000894W

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