Chiral Ruthenium Complexes of *N,N′*-Bis(diphenylphosphino) 1,2-Diamines

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Facile reactions of $[Ru_2(OAc)_4]$ with the bis(phosphino) diamines $Ph_2PN(Me)CH(R)CH(R)N(Me)PPh_2$ (**1a**−**c**: **a**, R = H; **b**, 2R = $-(CH_2)_4-$; **c**, R = Ph) affords Δ and Λ stereoisomers of $[Ru(OAc)_2(P,P)]$ (**2a**−**c**). In boiling THF, complex **2a** undergoes structural rearrangement, involving the sequential rupture of C−H, C−N, P−N, and C−O bonds. Under the same conditions **2c** gives a cyclometalated species, whereas **2b** is thermally stable.

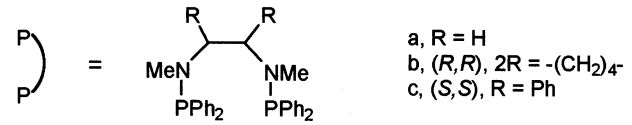
Introduction

Chiral bis(phosphino) diamines, prepared from the readily available enantiopure 1,2-diamines, have been extensively used as chiral auxiliaries in metal-catalyzed stereoselective organic transformations. Numerous Rh,[1] Pd,[2] and Pt[3] complexes of these ligands have been prepared and characterized. However, bis(phosphino) diamine−ruthenium complexes are scarce[4,5] and structural features, solution behavior, and the chemical properties of these species have been largely unexplored. We have recently reported that ruthenium acetate reacts with chiral aminophosphines to afford enantiomerically pure octahedral Ru complexes.[6] These results prompted us to investigate the reactivity of $[Ru_2(OAc)_4]$ toward bis(phosphino) diamines **1a**−**c** (Chart 1), and we now wish to report the structure, fluxional behavior, and thermal rearrangement of the resulting complexes.

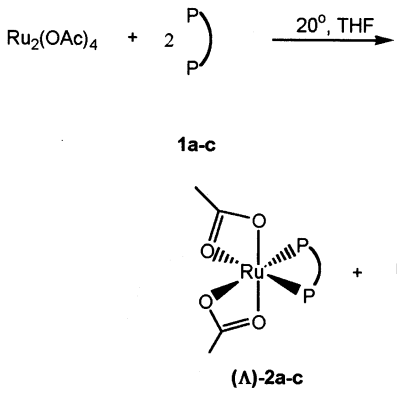
Results and Discussion

Reaction of 1a−c with $[Ru_2(OAc)_4]$. X-ray Structure of 2a,b. Fluxional Behavior of 2a−c. Treating $[Ru_2(OAc)_4]$ in THF with 1 equiv of **1a**−**c** at room temperature afforded the corresponding complexes **2a**−**c** (eq 1). According to the ^{31}P NMR spectra, the formation of **2a** occurred almost instantaneously, whereas bis(phosphino) diamines **1b**,**c** initially gave precipitates of unknown composition, which slowly (1−2 h) dissolved, and are completely converted into complexes **2b**,**c**.

Chart 1



1a-c



Complexes **2a**−**c** were isolated as air-stable crystalline solids and were characterized by elemental analysis and NMR spectroscopy (see Experimental Section). The solid-state structures of **2a**,**b** were established by single-crystal X-ray diffraction studies. Both complexes crystallize as 1:1 mixtures of Δ and Λ stereoisomers, as the asymmetric units of **2a**,**b** contain two independent molecules with opposite configurations of stereogenic Ru centers. ORTEP plots showing the stereoisomers of **2a**,**b** are given in Figures 1 and 2, with selected bond distances and angles presented in Tables 1 and 2, respectively.

The seven-membered chelate rings of **2a**,**b** adopt chiral conformations and are mirror images of each

(1) See for example: (a) Zhang, F.-Y.; Pai, C.-C.; Chan, A. S. C. *J. Am. Chem. Soc.* **1998**, *120*, 5808. (b) Roucox, A.; Suisse, I.; Devocelle, M.; Carpenter, J.-F.; Agbossou, F.; Mortreux, A. *Tetrahedron: Asymmetry* **1996**, *7*, 379. (c) Valentini, C.; Cernia, E.; Fiorini, M.; Giongo, G. M. *J. Mol. Catal.* **1984**, *23*, 81. (d) Onuma, K.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 761.

(2) See for example: (a) Balakrishna, M. S.; Walawalker, M. G. *J. Organomet. Chem.* **2001**, *628*, 76. (b) Ly, T. Q.; Slawin, A. M. Z.; Woolins, J. D. *J. Chem. Soc., Dalton Trans.* **1997**, 1611. (c) Kim, B.-J.; Yang, K.; Jung, M.-J.; Lee, B.-W.; Doh, M.-K. *Bull. Kor. Chem. Soc.* **1997**, *18*, 1162. (d) Benincori; T.; Brenna, E.; Sannicolo, F.; Trimarco, L.; Antognazza, P.; Cesarotti, E.; Demartin, F.; Pilati, T.; Zotti, G. *J. Organomet. Chem.* **1997**, *529*, 445.

(3) See for example: (a) Zhaofu, F.; Thonnessen, H.; Jones, P. G.; Crowe, L.; Harris, R. K.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1763. (b) Munzenberg, R.; Rademaker, P.; Boese, R. *J. Mol. Struct.* **1998**, *444*, 77. (c) Powell, J.; Lough, A.; Raso, M. *J. Chem. Soc., Dalton Trans.* **1994**, 1571. (d) Paine, N.; Stephan, D. W. *J. Organomet. Chem.* **1981**, *221*, 203.

(4) Abdur-Rashid, K.; Lough, A. J.; Morris, R. H. *Organometallics* **2001**, *20*, 1047.

(5) Balakrishna, M. S.; Abhyankar, R. M.; Mague, J. T. *J. Chem. Soc., Dalton Trans.* **1999**, 1407.

(6) Kuznetsov, V. F.; Yap, G. P. A.; Alper, H. *Organometallics* **2001**, *20*, 1300.

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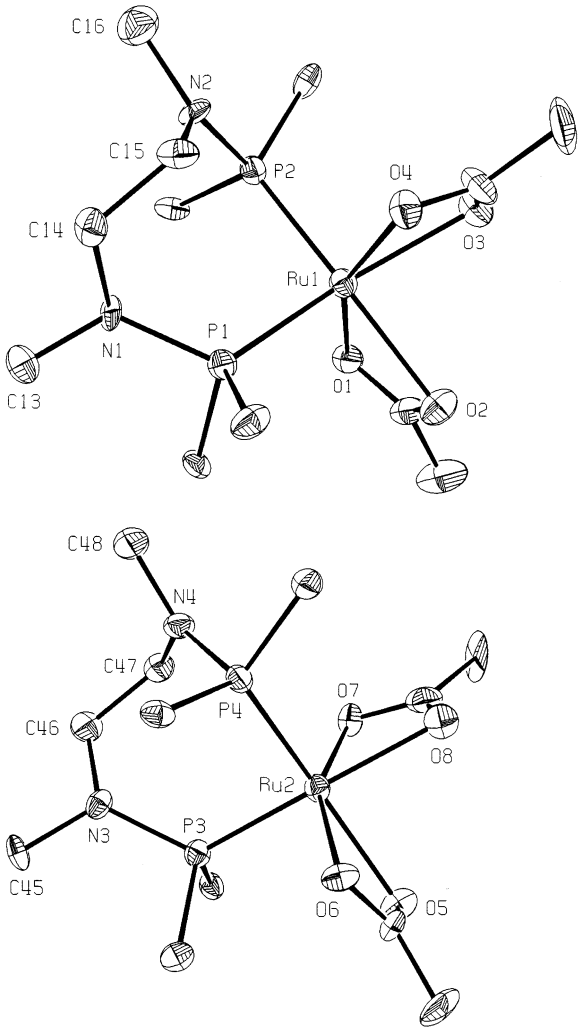


Figure 1. Perspective diagram showing Δ and Λ stereoisomers of **2a** with 30% probability ellipsoids. The hydrogen atoms and phenyl carbon atoms (except for ipso) are omitted.

other in (Δ)- and (Λ)-**1a**, whereas in (Δ)- and (Λ)-**1b** they are neither mirror images nor superimposable. Therefore, Δ and Λ stereoisomers of **2a** relate to each other as enantiomers, whereas (Δ)- and (Λ)-**2b** are diastereomeric in nature. The seven-membered chelate rings of both complexes are twisted in such a way that the two P atoms within each molecule are in different environments (cf. for example P(1)···C(15) = 3.139 Å vs P(2)···C(14) = 3.464 Å for (Δ)-**1a** or P(1)···C(19) = 3.764 Å vs P(2)···C(14) = 3.162 Å for (Δ)-**2b**) and therefore are chemically inequivalent.

The $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in toluene, recorded at −70 °C, shows two well-separated doublets. At higher temperatures, the signals broaden, coalesce at −43 °C, and finally transform to a sharp singlet at 20 °C (Figure 3). These data indicate that, as in the solid state, the two P atoms of **2a** are inequivalent in solution; however, the chelate ring of **2a** is conformationally nonrigid. The same is true for complexes **2b**,**c** (VT NMR spectra are shown in Figures 4 and 5); in this case (Δ)- and (Λ)-**2b**,**c** relate to each other as diastereomers and therefore give separate signals in the ^{31}P NMR spectra recorded below −70 °C (each stereoisomer appears as two doublets). According to the spectra, the fluxional behavior of **2a**−**c** involves two distinct processes: P_A/P_B site exchange and Δ/Λ interconversion. In general, two possible configurations of the stereogenic Ru center along with two different chiral conformations of the seven-membered chelate may afford four combinations. The X-ray diffraction data and VT NMR spectra, however, indicate that only two of the four possible stereoisomers exist in the solid state and in solution. Therefore, the two above-mentioned processes are apparently interrelated, so that the configuration of Ru centers in **2a**−**c** defines the conformation of the chelate cycles and vice versa.

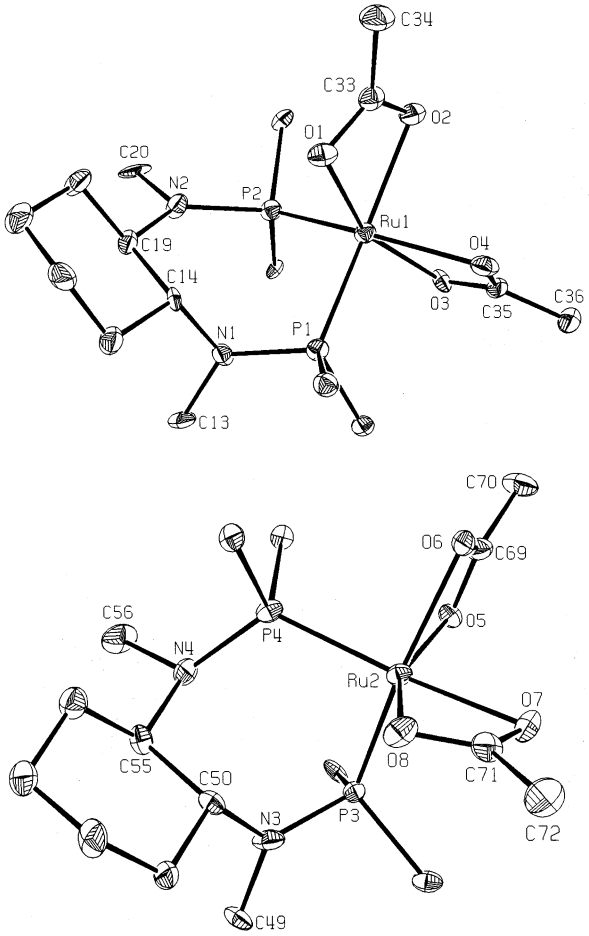


Figure 2. Perspective diagram showing Δ and Λ stereoisomers of **2b** with 30% ellipsoids. The hydrogen atoms and phenyl carbon atoms (except for ipso) are omitted.

Table 1. Selected Bond Distances (Å) and Angles (deg) for (Δ)-2a·$C_6H_8O_2$

Ru(1)−P(1)	2.236(4)	Ru(1)−O(2)	2.260(9)
Ru(1)−P(2)	2.216(4)	Ru(1)−O(3)	2.210(9)
Ru(1)−O(1)	2.113(8)	Ru(1)−O(4)	2.126(8)
P(1)−Ru(1)−O(3)	161.9(2)	P(1)−Ru(1)−P(2)	92.06(12)
P(2)−Ru(1)−O(2)	161.6(3)	O(1)−Ru(1)−O(2)	59.6(3)
O(1)−Ru(1)−O(4)	155.0(4)	O(3)−Ru(1)−O(4)	60.6(4)

Table 2. Selected Bond Distances (Å) and Angles (deg) for (Δ)-2b

Ru(1)−P(1)	2.216(2)	Ru(1)−O(2)	2.239(4)
Ru(1)−P(2)	2.198(16)	Ru(1)−O(3)	2.216(5)
Ru(1)−O(1)	2.102(5)	Ru(1)−O(4)	2.121(6)
P(1)−Ru(1)−O(3)	163.46(17)	P(1)−Ru(1)−P(2)	91.19(7)
P(2)−Ru(1)−O(2)	160.82(17)	O(1)−Ru(1)−O(2)	60.2(2)
O(1)−Ru(1)−O(4)	156.85(18)	O(3)−Ru(1)−O(4)	60.5(2)

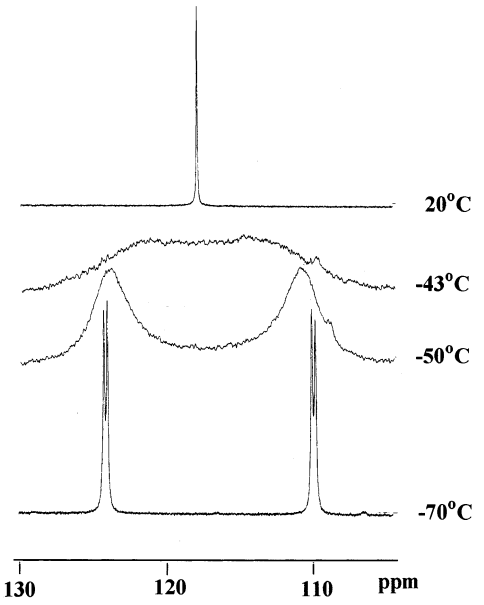


Figure 3. 201 MHz VT $^{31}P\{^1H\}$ NMR spectra of **2a** in toluene-d_8.

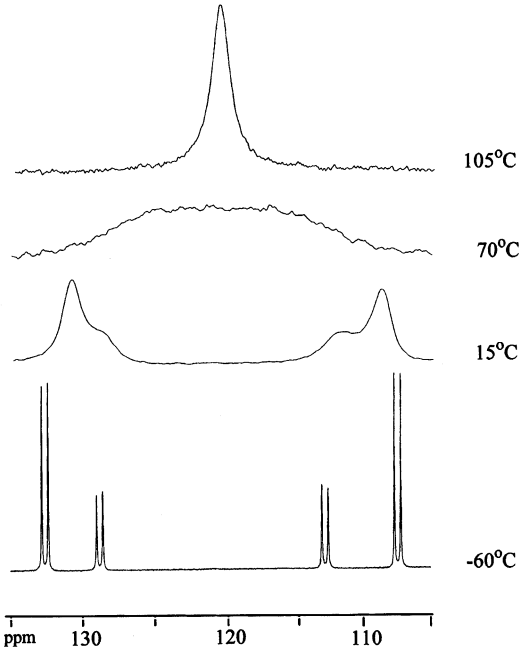


Figure 4. 201 MHz $^{31}P\{^1H\}$ VT NMR spectra of **2b** in toluene-d_8.

Thermal Rearrangement of 2a. Upon mild heating in solution, complex **2a** readily undergoes rearrangement to afford, according to ^{31}P NMR, complexes **3** (δ 82.2 (d, J = 40 Hz), 83.8 (d, J = 40 Hz)) and **4** (δ 80.5 (d, J = 46 Hz), 83.6 (d, J = 46 Hz)) in a 1:1 ratio. In boiling THF this transformation requires ca. 15 min for completion. Both complexes were isolated and characterized by elemental analysis and NMR spectroscopy. The solid-state structures of **3** and **4** were established by means of single-crystal X-ray diffraction.

The unit cell of crystalline **3** consists of 12 molecules; 6 of them possess the Δ configuration, while the others display the Λ configuration. The asymmetric unit of **3** contains either one Δ and two Λ or one Λ and two Δ stereoisomers. As the space group of the complex is centrosymmetric, the Δ,Λ,Λ and Λ,Δ,Δ motifs in the crystal are related to each other by the inversion center. Being crystallographically distinct, the two Δ or two Λ stereoisomers within each asymmetric unit are chemically identical; therefore, the ORTEP plot given in Figure 6 shows only two arbitrarily chosen molecules with opposite configuration. Selected bond distances and angles are presented in Table 3.

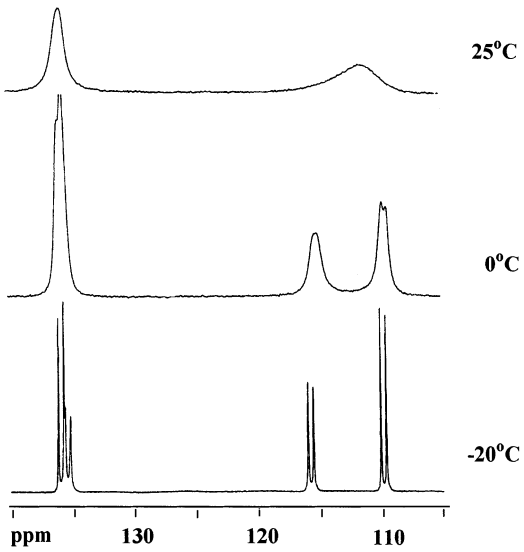


Figure 5. 201 MHz $^{31}P\{^1H\}$ VT NMR spectra of **2c** in toluene-d_8.

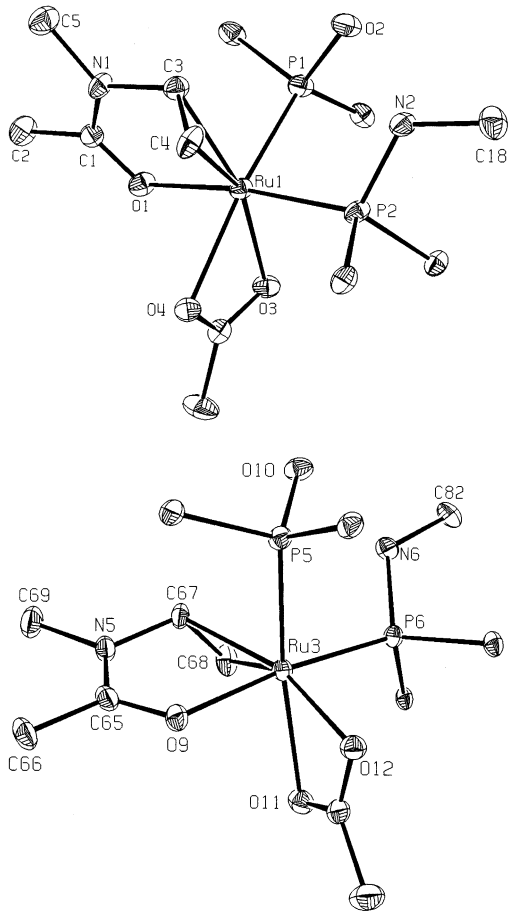


Figure 6. Perspective diagram showing Δ,*S* and Λ,*R* stereoisomers of **3** with 30% probability ellipsoids. The hydrogen atoms and phenyl carbon atoms (except for ipso) are omitted.

Table 3. Selected Bond Distances (Å) and Angles (deg) for (Λ,*R*)-3

Ru(1)−P(1)	2.3085(13)	Ru(1)−C(3)	2.131(4)
Ru(1)−P(2)	2.2833(12)	Ru(1)−C(4)	2.135(5)
Ru(1)−O(1)	2.127(3)	C(3)−C(4)	1.391(6)
Ru(1)−O(3)	2.147(3)	C(1)−O(1)	1.246(5)
Ru(1)−O(4)	2.249(3)	P(1)−O(2)	1.523(3)
P(1)−Ru(1)−P(2)	90.30(4)	O(1)−Ru(1)−O(4)	80.53(11)
P(1)−Ru(1)−O(1)	94.85(8)	O(1)−Ru(1)−C(4)	100.34(14)
P(1)−Ru(1)−O(3)	106.36(9)	O(4)−Ru(1)−C(4)	88.81(15)
P(1)−Ru(1)−C(4)	105.97(14)	P(2)−Ru(1)−C(4)	83.11(12)
O(1)−Ru(1)−O(3)	82.36(11)	N(1)−C(3)−C(4)	121.9(4)

Table 4. Selected Bond Distances (Å) and Angles (deg) for (Λ,*S*)-4·MeOH

Ru(1)−P(1)	2.318(3)	Ru(1)−C(3)	2.055(8)
Ru(1)−P(2)	2.280(3)	Ru(1)−C(4)	2.204(7)
Ru(1)−O(1)	2.115(5)	C(3)−C(4)	1.395(11)
Ru(1)−O(3)	2.148(5)	C(1)−O(1)	1.262(10)
Ru(1)−O(4)	2.214(5)	P(1)−O(2)	1.514(6)
P(1)−Ru(1)−P(2)	95.51(9)	O(1)−Ru(1)−O(4)	84.7(2)
P(1)−Ru(1)−O(1)	92.41(17)	O(1)−Ru(1)−C(4)	95.4(3)
P(1)−Ru(1)−O(3)	100.00(17)	O(4)−Ru(1)−C(4)	122.5(2)
P(1)−Ru(1)−C(4)	77.3(2)	P(2)−Ru(1)−C(4)	87.8(2)
O(1)−Ru(1)−O(3)	84.17(19)	N(1)−C(3)−C(4)	117.4(7)

The distorted-octahedral coordination environment of the central Ru atom in **3** consists of diphenylphosphine oxide attached to the metal by a σ-P−Ru bond, a bidentate acetate, diphenyl(methylamino)phosphine, and *N*-methyl-*N*-vinylacetamide, coordinated to Ru by the C−C double bond and oxygen. The internal olefinic carbons of the complex are stereogenic and possess opposite configurations in the Λ and Δ stereoisomers (*R* and *S*, respectively). The complex **3** therefore is a racemic mixture of Λ,*R* and Δ,*S* enantiomers.

In contrast to the case for **3**, the asymmetric unit of crystalline **4**·MeOH contains a single enantiomer. An ORTEP plot of the complex is shown in Figure 7, and selected bond distances and angles are given in Table 4. The coordination environment of the central Ru atom in complex **4** is formed by the same ligands as those in **3**. The internal olefinic carbon of the *N*-methyl-*N*-vinylacetamido ligand possesses the *S* configuration, while the central Ru atom is in a Λ configuration. Even though X-ray analysis shows the presence of only one stereoisomer in the single crystal of **4**·MeOH, the isolated complex is not optically active. It is conceivable therefore that **4** is indeed a racemic mixture of Λ,*S* and Δ,*R* enantiomers which crystallize separately. Thus, thermal rearrangement of **2a** affords four stereoisomers of acetoxy(diphenylphosphinito-*P*)(η^2-*N*-methyl-*N*-vinylacetamido)(*N*-methyldiphenylphosphinamide-*P*)ruthenium (**3** and **4**); complexes **4** and **3** relate to each other as epimers, and both are 1:1 mixtures of enantiomers.

Although the detailed mechanism for the formation of **3** and **4** remains unknown, the reaction certainly includes a series of C−H, C−N, P−N, and C−O bond cleavage processes. A possible sequence of events is shown in Scheme 1. Oxidative addition of the aliphatic C−H bond of the coordinated bis(phosphino) diamine may be followed by reductive elimination of acetic acid. Subsequent protonation of an amino group of the resulting four-membered P−N−C−Ru cycle promotes the C−N bond rupture accompanied by a 1,2-hydrogen shift to give (methylamino)diphenylphosphine coordinated to Ru via phosphorus and a chelating (methylvinylamino)diphenylphosphine. The latter ligand undergoes attack by an acetate anion, which may occur via a four-membered intermediate state similar to that proposed for the well-known Wittig reaction to afford **3** and **4**. It is remarkable that this multistep, complex rearrangement occurs under very mild conditions and proceeds with high selectivity (^{31}P NMR yield of **3** and **4** is ca. 95%). Although aliphatic C−H bond activation in coordinated diphosphines, leading to the formation of cyclometalated, olefinic, or carbene complexes, is a well-known process,[7] we are not aware of any transformations of bis(phosphino) diamine ligands, accompanied by activation and cleavage of P−N and C−N bonds.

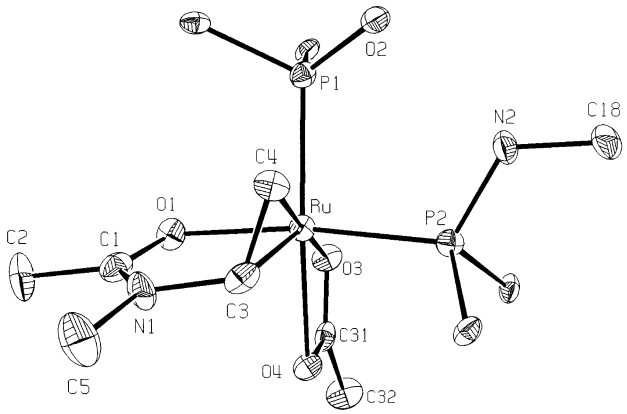


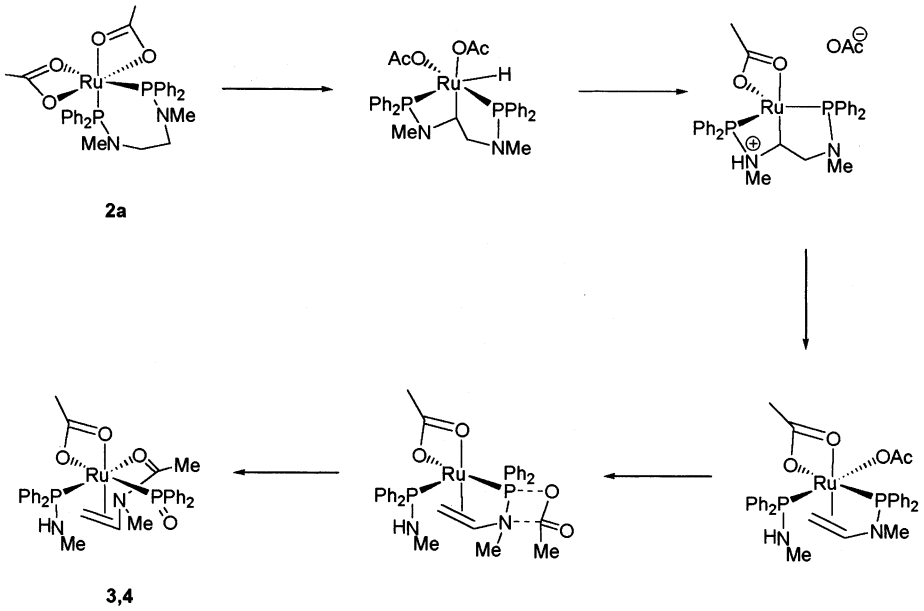
Figure 7. Perspective diagram of **4** with 30% probability ellipsoids. The hydrogen atoms and phenyl carbon atoms (except for ipso) are omitted.

According to ^{31}P NMR spectroscopy, the isolated **3** or **4** can be kept in solution at room temperature for 1 week without any signs of decomposition or racemization. However, at elevated temperature both complexes undergo slow epimerization to afford a mixture of **3** and **4** in a ca. 1:3 ratio. In boiling dioxane, this ratio is reached in 3−4 h and then remains constant upon prolonged (up to 12 h) heating. Thus, complex **4** is thermodynamically more stable than **3** and therefore formation of both complexes in equimolar amounts upon thermal rearrangement of **2a** is kinetically controlled.

Thermochemical Behavior of 2b,c. X-ray Structure of Cyclometalated Complex 5. In contrast to **2a**, complex **2b** does not undergo rearrangement or noticeable decomposition when heated in boiling THF or benzene for 2 h. In boiling toluene slow decomposition (ca. 10% in 4 h) leading to a complex mixture of unidentified products was observed by ^{31}P NMR. Since the electronic properties of **1a** and **1b** are very similar, the superior thermal stability of **2b** is probably attributable to steric factors. Due to the presence of a cyclohexane ring, incorporated into the seven-membered chelate, the latter may not be able to adopt the conformation required for the oxidative addition of C−H bond to the ruthenium center.

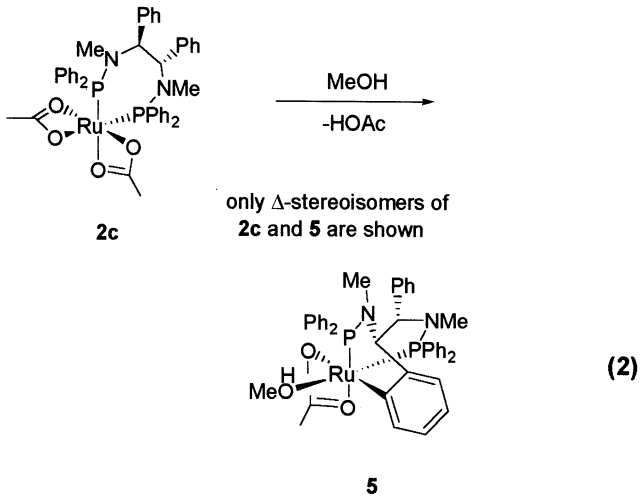
(7) See for example: (a) Vigalok, A.; Milstein, D. *Organometallics* **2000**, *19*, 2061. (b) McLoughlin, M. A.; Flesher, R. J.; Kaska, W. C. *Organometallics* **1994**, *13*, 3816. (c) Errington, R. J.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc. Dalton Trans.* **1982**, 1829. (d) Bennett, M. A.; Newmann, H. *Aust. J. Chem.* **1980**, *33*, 1251.

Scheme 1[a]



[a] Only Δ stereoisomers of **2a**, **3**, and **4** are shown.

Heating **2c** in boiling methanol afforded complex **5** (eq 2). According to ^{31}P NMR, the complete transformation takes ca. 15 min. The complex was isolated as air-stable yellow crystals (1:1 methanol solvate) and characterized by elemental analysis and NMR spectroscopy (see Experimental Section). The solid-state structure of **5**·MeOH was established by single-crystal X-ray diffraction.



(2)

The asymmetric unit of crystalline **5**·MeOH contains two molecules of the complex possessing opposite configurations of stereogenic Ru centers. The ORTEP plot showing both molecules is given in Figure 8. Selected bond lengths and angles are presented in Table 5.

The central Ru atom of the complex assumes a distorted-octahedral coordination geometry. The bis(amino)phosphine ligand spans three facial positions of the octahedron and is attached to Ru via two phosphorus atoms and by an ortho-metalated phenyl ring. The remaining positions around the metal are occupied by a molecule of methanol and by the bidentate acetate ligand. Although the methanolic hydrogen could not be located by the X-ray analysis, we believe that **5** indeed contains coordinated MeOH rather than a methoxy ligand, as in the latter case the complex would have to be paramagnetic.

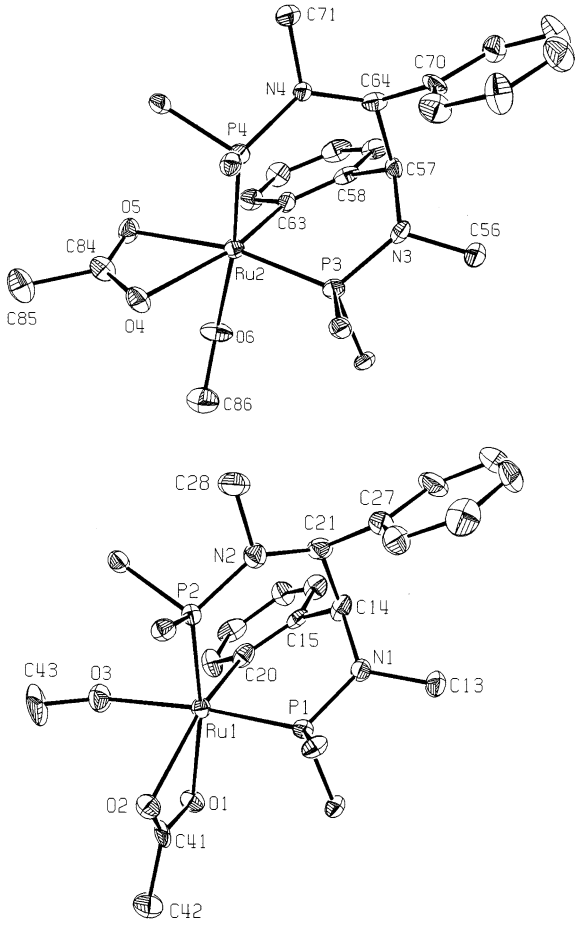


Figure 8. Perspective diagram showing Δ and Λ stereoisomers of **5** with 30% probability ellipsoids. The hydrogen atoms and non-ipso phenyl carbon atoms of PPh_2 groups are omitted.

Table 5. Selected Bond Distances (Å) and Angles (deg) for (Δ)-5·MeOH

Ru(1)−P(1)	2.192(3)	Ru(1)−O(2)	2.341(7)
Ru(1)−P(2)	2.203(3)	Ru(1)−O(3)	2.267(7)
Ru(1)−O(1)	2.219(7)	Ru(1)−C(20)	2.037(10)
P(1)−Ru(1)−P(2)	90.23(10)	P(2)−Ru(1)−O(3)	95.2(2)
P(1)−Ru(1)−C(20)	89.6(3)	O(1)−Ru(1)−O(2)	57.6(2)
P(2)−Ru(1)−C(20)	91.1(3)	O(2)−Ru(1)−O(3)	80.5(3)
P(2)−Ru(1)−O(2)	113.96(18)	C(20)−Ru(1)−O(3)	92.5(4)

The $^{31}P\{^1H\}$ NMR spectrum of **5**·MeOH in CD_2Cl_2, recorded at 20 °C, shows two sharp doublets. The signals gradually broaden with a decrease in temperature, but they neither split nor coalesce, even at −100 °C. These observations suggest that in solution Δ,*S*,*S* and Λ,*S*,*S* epimers of **5** may undergo an interconversion, which remains fast even at low temperatures. ^1H and ^{13}C NMR spectra of **5**·MeOH show that the coordinated and cocrystallized methanol molecules are indistinguishable in solution and therefore exchange rapidly. Perhaps in solution the MeOH ligand dissociates from the Ru center and the complex **5** exists as a stereochemically nonrigid coordinatively unsaturated species or as a solvento complex.

Conclusions

Ruthenium complexes of general formula $[Ru(OAc)_2(P,P)]$ can be readily prepared from ruthenium acetate and bis(phosphino) diamines **1a**−**c**. The complexes crystallize as 1:1 mixtures of Δ and Λ stereoisomers, which undergo fast interconversion in solution. The seven-membered chelate cycle of **2a**−**c** can adopt two distinct conformations, which are defined by the configuration of stereogenic Ru centers. The presence of chiral centers in the backbone of **2b**,**c** only slightly affects the relative thermodynamic stability of Δ and Λ epimers, as both stereoisomers are present in solution in a (1:1)−(1:2) ratio.

The C−H bonds of coordinated **1a**,**c** readily undergo oxidative addition to Ru centers of **2a**,**c**, which leads to a novel and complicated rearrangement or results in the formation of cyclometalated species. The superior stability of **2b** is apparently a consequence of the enhanced rigidity of the seven-membered chelate cycle fused with the cyclohexane ring.

Experimental Section

All manipulations were carried out under inert atmosphere using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. $[Ru_2(OAc)_4]$·2THF,[6] *N*,*N*′-bis(diphenylphosphino)-*N*,*N*′-dimethylethylenediamine (**1a**)[2a] and (1*R*,2*R*)-bis((diphenylphosphino)methylamino)cyclohexane (**1b**)[8] were prepared as reported elsewhere. Other chemicals were purchased from Aldrich or Strem and were used as received. The following instruments were used: Varian XL-300 (NMR), Bruker AMX 500 (VT NMR), Perkin-Elmer 2400 Series II (combustion microanalysis), and Perkin-Elmer 241 polarimeter.

Synthesis of (1*S*,2*S*)-*N*,*N*′-Bis(diphenylphosphino)-*N*,*N*′-dimethyl-1,2-diphenylethylenediamine (1c). The compound was prepared by modification of the published procedure.[9] A stirred solution of (1*S*,2*S*)-$[PhCH(NH_2)]_2$ (3.67 g, 17.28 mmol) in THF (150 mL) was cooled to 0 °C and treated with K_2CO_3 (6 g) in water (20 mL) and then with ClCOOEt (10 mL). The resulting two-phase mixture was stirred at ambient temperature for 4 h. The upper layer was separated and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (ca. 80 mL), and the solution was dried over Na_2SO_4, filtered, evaporated, and dried under vacuum at 100 °C to give 6.12 g (17.2 mmol, 99%) of (1*S*,2*S*)-$[PhCH(NHCOOEt)]_2$ as a snow white crystalline solid.

Solid (1*S*,2*S*)-$[PhCH(NHCOOEt)]_2$ (6.1 g, 17.11 mmol) was added to a stirred solution of $LiAlH_4$ (2.0 g, 52.7 mmol) in THF (60 mL) at 0 °C. The mixture was stirred at ambient temperature for 1 h and then heated to reflux overnight, cooled to 0 °C, and treated subsequently (*Caution!*) with water (4 mL) and 15% NaOH (3 mL). The resulting suspension was stirred at ambient temperature for 1 h, heated to reflux, and filtered while hot. The white precipitate on the filter was washed with THF (3 × 10 mL), and the combined filtrates were evaporated to dryness. The residue was dissolved in pentane (20 mL) and the resulting solution filtered. The filtrate was evaporated to give (1*S*,2*S*)-$[PhCH(NHMe)]_2$ (3.60 g 14,97 mmol, 87%) as a white crystalline solid.

A stirred mixture of (1*S*,2*S*)-$[PhCH(NHMe)]_2$ (3.50 g, 14.57 mmol), benzene (60 mL), Et_3N (6 mL), and Ph_2PCl (5.8 mL, 7.0 g, 31.77 mmol) was heated to reflux for 48 h and filtered while hot. The white precipitate on the filter was washed with hot benzene (3 × 20 mL), and the combined filtrates were evaporated to dryness. The residue was dissolved in warm benzene (40 mL), passed through a short column with basic alumina (40 × 25 mm), and eluted with benzene (30 mL). The resulting solution was concentrated to ca. 20 mL and left overnight. The crystals that formed (long, thin, colorless needles) were separated by decantation, washed with pentane (2 × 10 mL), and dried under vacuum to give 6.25 g of a snow white solid. An additional 617 mg of product was isolated upon concentration of the mother liquor. The total yield of **1c** was 6.87 g (77%). The compound is air stable in the solid state and can be stored in air. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 65.5 (s). ^1H NMR ($CDCl_3$): δ 2.70 (d, J = 2.7 Hz, 6H); 5.30 (m, 2H); 6.76 (t, J = 8 Hz, 4H); 7.04−7.39 (m, 26H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.04 (d, J = 11 Hz, Me); 31.07 (d, J = 11 Hz, Me); 68.68 (d, J = 12 Hz, CH); 69.22 (d, J = 12 Hz, CH); 126.89−139.46 (18 lines, Ph). $[\alpha]_D^{20} = -162.7°$ (c = 2.7, CH_2Cl_2).

Synthesis of 2a. Solid **1a** (901 mg, 1.974 mmol) was added to a solution of $[Ru_2(OAc)_4]$·2THF (552 mg, 0.948 mmol) in THF (20 mL), and the mixture was stirred at room temperature for 5 min. The resulting clear orange solution was set aside for 2 h. The formed voluminous precipitate was filtered, washed with cold THF (5 mL) and cold Et_2O (5 mL), and dried under vacuum to give 742 mg of **2a**·THF as a pale yellow powder. An additional 280 mg of the complex was isolated upon concentration of the mother liquor. The total yield was 1022 mg (1.367 mmol, 72%). Anal. Calcd for $C_{36}H_{44}N_2O_5P_2Ru$: C, 57.82; H, 5.93; N, 3.75. Found: C, 57.48; H, 5.65; N, 4.12. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 118 (s). ^1H NMR ($CDCl_3$, 20 °C): δ 1.4 (s, 6H); 1.8 (m, 4H, THF); 2.65 (t, J = 6.5 Hz, 6H); 3.2 (broad, 4H); 3.7 (m, 4H, THF); 7.3 (broad, 20H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 23.3 (s, CH_3); 25.6 (s, THF); 40.4 (t, J = 5 Hz, CH_3); 52.2 (vt, ^vJ = 5 Hz, CH_2); 67.9 (s, THF); 127.4 (vt, ^vJ = 5 Hz, Ph); 128.9 (broad, Ph); 132.1 (broad, Ph); 135.3 (broad m, Ph); 187.2 (s, OAc).

Synthesis of 4·MeOH. A stirred suspension of **2a**·THF (642 mg, 0.858 mmol) in THF (10 mL) was heated to reflux for 30 min, and the resulting clear orange solution was evaporated to dryness. The residue was dissolved in warm MeOH (5 mL) and left overnight at room temperature. The precipitated pale yellow crystals were separated by decantation, washed with cold MeOH (2 × 2 mL), and dried under vacuum to give 174 mg of **4**·MeOH. An additional 43 mg of the complex was isolated upon concentration of mother liquor. The total yield was 217 mg (0.307 mmol, 36%). Anal. Calcd

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Table 6. Summary of Crystallographic Data for 2a·2$C_4H_8O_2$, 2b, 3, 4·MeOH, and 5·MeOH

	1a·2$C_4H_8O_2$	**2b**	**3**	**4**·MeOH	**5**·MeOH
formula	$C_{36}H_{44}N_2O_6P_2Ru$	$C_{36}H_{42}N_2O_4P_2Ru$	$C_{32}H_{35}N_2O_4P_2Ru$	$C_{33}H_{39}N_2O_5P_2Ru$	$C_{44}H_{48}N_2O_4P_2Ru$
fw	763.74	729.73	674.63	706.67	831.85
cryst dimens, mm	0.4 × 0.08 × 0.08	0.2 × 0.1 × 0.1	0.4 × 0.3 × 0.2	0.1 × 0.1 × 0.1	0.3 × 0.2 × 0.1
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
a, Å	37.947(9)	18.121(2)	21.405(4)	9.404(8)	10.499(1)
b, Å	8.594(2)	9.9900(8)	12.474(2)	15.899(9)	19.159(2)
c, Å	30.359(9)	19.152(2)	34.097(6)	11.373(9)	20.174(3)
β, deg	128.634(4)	97.449(1)	98.897(3)	105.64(2)	98.903(2)
space group	*C*2	$P2_1$	$P2_1/c$	$P2_1$	$P2_1$
Z	8	4	4	2	4
V, Å^3	7734(4)	3437.7(5)	2467(2)	1638(1)	4009.0(9)
d_{calcd}, g/cm^3	1.312	1.410	1.495	1.433	1.378
T, K	238(2)	296(2)	238(2)	238(2)	236(2)
radiation (λ)			Mo Kα (0.710 73 Å)		
abs coeff, mm^{-1}	0.531	0.590	0.670	0.619	0.515
transmissn (max/min)	1.69242	1.29608	2.09762	1.75744	1.14644
$R(F)$,%[a]	6.06	3.94	4.93	4.37	5.03
$R(wF^2)$,%[a]	16.26	7.12	10.18	7.35	14.31
GOF	1.024	1.040	1.017	1.008	1.062
Flack param	0.04(6)	−0.03(3)	n/a	−0.01(4)	−0.05(4)

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

for $C_{33}H_{40}N_2O_5P_2Ru$: C, 56.01; H, 5.70; N, 3.96. Found: C, 56.37; H, 5.48; N, 4.12. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 82.2 (d, J = 39.5 Hz); 86.5 (d, J = 39.5 Hz). ^1H NMR ($CDCl_3$, 20 °C): δ 1.35 (s, 3H); 1.55 (s, 3H); 1.9 (m, 1H); 2.1 (dd, J_1 = 5.5 Hz, J_2 = 11 Hz, 3H); 2.55 (s, 3H); 2.6 (m, 1H); 3.4 (s, 3H, MeOH); 3.75 (broad, 1H, MeOH); 4.2 (dd, J_1 = 6 Hz, J_2 = 7.5 Hz, 1H); 6.75 (m, 2H); 6.9 (m, 2H); 7.1 (m, 5H); 7.35 (m, 6H); 7.55 (m, 2H); 7.8 (m, 2H); 8.1 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 19.5 (d, J = 3 Hz, CH_3); 23.8 (s, CH_3); 28.5 (d, J = 9.5 Hz, CH_3); 38.1 (s, CH_3); 44.5 (d, J = 7.5 Hz, CH_2); 50.1 (s, MeOH); 88.8 (s, CH); 126.5−143.5 (32 lines, Ph); 177.1 (s, C═O); 186.5 (s, C═O).

Synthesis of 3. A stirred mixture of $[Ru_2(OAc)_4]$·2THF (538 mg, 0.923 mmol), **1a** (851 mg, 1.864 mmol), and THF (20 mL) was heated to reflux for 30 min, and the orange solution that formed was evaporated to dryness. The residue was stirred with benzene (10 mL); the resulting suspension was heated to reflux for 30 min and cooled to room temperature to give a yellow precipitate of crude **4** and an orange solution. The mixture was filtered, and the pale yellow precipitate was washed with benzene (2 × 2 mL). The combined filtrates were concentrated to ca. 8 mL and set aside for 2 h to give an additional amount of crude **4**, which was separated by decantation and washed with benzene (2 mL). The combined mother liquor and washings were diluted with heptane (5 mL), reduced in volume to ca. 10 mL under vacuum, and left overnight at room temperature. The formed orange crystals were separated by decantation, washed with pentane (2 × 4 mL), and dried under vacuum to give **3** (320 mg, 0.474 mmol, 26%). Anal. Calcd for $C_{32}H_{36}N_2O_4P_2Ru$: C, 56.88; H, 5.37; N, 4.15. Found: C, 57.25; H, 5.41; N, 4.01. $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 81.4 (d, J = 46 Hz); 83.7 (d, J = 46 Hz). ^1H NMR (C_6D_6, 20 °C): δ 0.85 (s, 3H); 1.65 (s, 3H); 1.8 (s, 3H); 2.25 (dd, J_1 = 5.5 Hz, J_2 = 11 Hz, 3H); 2.85 (dd, J_1 = 6 Hz, J_2 = 8.5 Hz, 1H); 3.15 (d, J = 8.5 Hz, 1H); 5.15 (m, 1H); 6.8 (m, 1H); 6.9 (m, 3H); 7.0 (m, 3H); 7.15 (m, 2H); 7.25 (m, 2H); 7.3 (m, 4H); 8.15 (t, J = 8.5 Hz, 2H); 8.2 (t, J = 8 Hz, 2H); 8.65 (t, J = 8.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 19.7 (d, J = 4 Hz, CH_3); 23.9 (s, CH_3); 29. 5 (d, J = 10 Hz, CH_3); 38.1 (s, CH_3); 49.2 (s, CH_2); 86.2 (d, J = 9.5 Hz, CH); 124.5−145.4 (27 lines, Ph); 175.1 (d, J = 2 Hz, C═O); 186.8 (s, C═O).

Synthesis of 2b. Solid **1b** (487 mg, 0.954 mmol) was added to a stirred solution of $[Ru_2(OAc)_4]$·2THF (278 mg, 0.477 mmol) in THF (15 mL), resulting in the formation of a red-brown solution and a voluminous precipitate. The reaction mixture was stirred until all solids dissolved (ca. 1 h), and the resulting orange solution was reduced in volume to ca. 2 mL under vacuum, diluted with Et_2O (15 mL), and set aside for 2 h. The formed crystals were washed with Et_2O (2 × 5 mL) and dried under vacuum to give 662 mg (0.908 mmol, 95%) of **2b** as an orange microcrystalline solid. Anal. Calcd for $C_{36}H_{42}N_2O_4P_2Ru$: C, 59.25; H, 5.80; N, 3.84. Found: C, 59.28; H, 5.97; N, 3.65. $^{31}P\{^1H\}$ NMR (toluene-d_8, −80 °C): δ 109.3 (d, J = 53 Hz); 113.4 (d, J = 51 Hz); 129.9 (d, J = 51 Hz); 132.9 (d, J = 53 Hz). $[\alpha]_D^{20}$ = 68.8° (c = 0.64, MeOH).

Synthesis of 2c. CH_2Cl_2 (10 mL) was added to a mixture of $[Ru_2(OAc)_4]$·2THF (312 mg, 0.535 mmol) and **1c** (652 mg, 1.071 mmol), resulting in immediate formation of a burgundy solution and a dark red precipitate. The reaction mixture was stirred at room temperature for 1−2 h until all solids dissolved. The resulting dark orange solution was evaporated under vacuum, and the residue was dissolved in Et_2O (20 mL) to give a clear orange solution, which starts precipitating yellow crystals immediately. The solution was kept at room temperature for 2 h; the crystals were separated by decantation, washed with Et_2O (2 × 5 mL), and dried under vacuum to give 610 mg (0.737 mmol, 69%) of **2c**. An additional 197 mg of **2c** contaminated by ca. 10% of complex **5** (^{31}P NMR) was isolated upon the concentration of the mother liquor. Anal. Calcd for $C_{44}H_{44}N_2O_4P_2Ru$: C, 63.84; H, 5.36; N, 3.38. Found: C, 64.11; H, 5.42; N, 3.52. $^{31}P\{^1H\}$ NMR (THF, −80 °C): δ 111.5 (d, J = 53.5 Hz); 117.2 (d, J = 52 Hz); 136.4 (d, J = 52 Hz); 136.8 (d, J = 53.5 Hz). $[\alpha]_D^{20}$ = 37° (c = 0.64, MeOH).

Synthesis of 5·MeOH. A stirred suspension of **2c** (582 mg, 0.703 mmol) in THF (15 mL) was heated to reflux for 30 min. The resulting dark orange solution was evaporated; the residue was dissolved in warm MeOH (15 mL) and set aside for 2 h. The precipitated crystals were separated by decantation, washed with MeOH (2 × 4 mL), and dried under vacuum to give 478 mg of **5**·MeOH as a yellow microcrystalline solid. An additional 117 mg of the complex was isolated upon concentration of the mother liquor. The total yield of **5**·MeOH was 556 mg (0.668 mmol, 95%). Anal. Calcd for $C_{44}H_{48}N_2O_4P_2Ru$: C, 63.54; H, 5.82; N, 3.37. Found: C, 63.48; H, 5.72; N, 3.52. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 123.2 (d, J = 60 Hz); 127.5 (d, J = 60 Hz). ^1H NMR (CD_2Cl_2, 20 °C): δ 1.2 (broad, 2H); 1.7 (s, 3H); 1.9 (d, J = 8 Hz, 3H); 2.1 (d, J = 7 Hz, 3H); 3.2 (s, 6H); 4.2 (m, 2H); 6.6−7.8 (m, 29H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 23.8 (s, CH_3); 42.8 (d, J = 5 Hz, CH_3); 45.2 (d, J = 4.5 Hz, CH_3); 50.5 (s, CH_3); 76.1 (d, J = 5 Hz, CH); 79.8 (dd, J_1 = 10 Hz, J_2 = 3.5 Hz, CH); 120.4−138.8 (25 lines, Ph); 145.1 (d, J = 7.5 Hz, Ph); 151.8 (dd, J_1 = 10 Hz, J_2 = 2 Hz, Ph); 162.4 (t, J = 15 Hz, Ph); 184.6 (s, OAc). $[\alpha]_D^{20}$ = 162.7° (c = 0.3, MeOH).

Single-Crystal X-ray Diffraction Study of 2a·2$C_4H_8O_2$, 2b, 3, 4·MeOH, and 5·MeOH. Crystals suitable for X-ray analysis were obtained by slow crystallization of the corre-

sponding complexes from concentrated solutions in dioxane (**2a**·$2C_4H_8O_2$ and **2b**), benzene (**3**), or methanol (**4**·MeOH and **5**·MeOH). The crystals were mounted on thin glass fibers using viscous oil and cooled to the data collection temperatures. Data were collected on a Brucker AX SMART 1k CCD diffractometer using 0.3° *w* scans at 0, 90, and 180° in ϕ. A summary of the crystallographic details is given in Table 6. Initial 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.[10] Systematic absences in the diffraction data and unit-cell parameters were consistent with $P2_1$ (No. 4) and $P2_1/m$ (No. 11) for **4**·MeOH, **5**·MeOH, and **2b**, with $C2$ (No. 5), Cm (No. 8), and $C2/m$ (No. 12) for **2a**, and, uniquely, with $P2_1/c$ (No. 14) for **3**. All ambiguous space group options were explored, and only those reported herein yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. Symmetry-unique solvent molecules were located in each asymmetric unit of **4**·MeOH (one methanol molecule), **5**·MeOH (two methanol molecules), and **2a** (four-half-occupied dioxane molecules, two of which are at 2-fold axes). Refinement of the Flack parameter in all noncentrosymmetric solutions yielded nothing, indicating that the true hand of each data set was determined.

All non-hydrogen atoms were refined with anisotropic displacement coefficients, excluding the atoms of the cocrystallized dioxane in **2a**, which were refined isotropically. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHELXTL 6.12 program library.[11] ORTEP plots were made using ORTEP-III (1.0.3) software[12] downloaded from the Internet at http://www.chem.gla.ac.uk/~louis/ortep3.

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Supporting Information Available: Tables giving atomic coordinates, bond distances and angles, and isotropic and anisotropic thermal parameters and figures giving additional views of **2a**·$2C_4H_8O_2$, **2b**, **3**, **4**·MeOH, and **5**·MeOH. This material is available free of charge via the Internet at http://pubs.acs.org.

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