Synthesis and Structure of the Chiral Dihydrogen Complex *trans*-[Ru(η^2-H_2)H(R,R′-Me-DuPHOS)$_2$]PF_6 and the Dinitrogen Complex *trans*-[Ru(N_2)H(R,R′-Me-DuPHOS)$_2$]PF_6 (R,R′-Me-DuPHOS = 1,2-Bis((2*R*,5*R*)-2,5-dimethylphospholano)benzene)

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The complex [RuH(NH_2NMe_2)$_3$(cod)]PF_6, cod = cyclooctadiene, a ruthenium hydride synthon, reacts with 2 equiv of R,R′-Me-DuPHOS, 1,2-bis((2*R*,5*R*)-2,5-dimethylphospholano)-benzene, to produce the five-coordinate complex [RuH(R,R′-Me-DuPHOS)$_2$]PF_6. With H_2(g) this complex reversibly forms the dihydrogen complex *trans*-[Ru(η^2-H_2)H(R,R′-Me-DuPHOS)$_2$]-PF_6. The T_1(min) at 400 MHz of 9.0 ± 0.5 ms corresponds to an H−H distance of 0.78 Å for fast motion of the η^2-H_2 ligand or 0.99 Å for slow motion. The J(H,D) coupling value of the η^2-HD isotopomer is 30 Hz. By use of an empirical relationship this corresponds to an H−H distance of 0.92 Å. The structure of *trans*-[Ru(η^2-H_2)H(R,R′-Me-DuPHOS)$_2$]PF_6 was determined by X-ray. It has approximate C_2 symmetry in the solid state and in solution. The η^2-H_2 ligand is located in a *chiral pocket* defined by the diphosphine ligands. The five-coordinate complex reacts with N_2 (1 atm) at −30 °C to give the thermally unstable complex *trans*-[Ru(N_2)H(R,R′-Me-DuPHOS)$_2$]PF_6, which was characterized by IR, NMR, elemental analysis, and X-ray diffraction.

Introduction

The amplification of chiral information by transition metal catalysts is a cornerstone of asymmetric synthesis on a laboratory and industrial scale.[1] Ruthenium and rhodium hydride complexes that bear chiral phosphine ligands represent an important class of these catalysts and are employed in a variety of enantioselective homogeneous hydrogenations.[2,3] Two of the most successfully used chiral phosphine ligands are the BINAP ligand, BINAP = *R*/*S*-bis(diphenylphosphino)-1,1′-binaphthyl, introduced by Noyori[4,5] and the DuPHOS system developed by Burk and co-workers (Figure 1).[6−9] The catalytically active species in these systems is thought to have 1:1 stoichiometry of metal to diphosphine ligand with other coordination sites being occupied by hydride ligands and substrate or solvent molecules.[9,10]

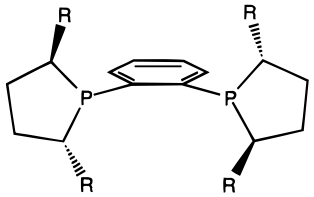

Figure 1. Structure of the DuPHOS ligand.

Detailed structural information on the coordination of the chiral phosphine to the metal is valuable for a thorough understanding of the steric interactions that lead to the observed high enantiomeric excess yield in catalytic homogeneous hydrogenation reactions with these complexes. The single crystal X-ray structure determinations of several ruthenium−BINAP and rhodium−DuPHOS catalyst precursors with a 1:1 stoichiometry are available in the literature,[11−14] but so far no example of a ruthenium−DuPHOS complex has been described.[15]

The 5-coordinate ruthenium complex [RuH(BINAP)$_2$]-PF_6 **(1)** with a 1:2 stoichiometry has also been used as

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(1) Nugent, W. A.; RajanBabu, T. V.; Burk, M. J. *Science* **1993**, *259,* 479−483.
(2) Noyori, R. *Asymmetric Catalysis in Organic Chemistry*; John Wiley & Sons: New York, 1994.
(3) Ojima, I. *Catalytic Asymmetric Synthesis*; VCH: Weinheim, Germany, 1993.
(4) Miyashita, A.; Takaya, H.; T. Souchi; Noyori, R. *Tetrahedron* **1984**, *40,* 1245−1253.
(5) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23,* 345−350.
(6) Burk, M. J.; Feaster, J. E.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1993**, *115,* 10125−10138.
(7) Burk, M. J.; Feaster, J. E.; Harlow, R. L. *Tetrahedron: Asym.* **1991**, *2,* 569−592.
(8) Burk, M. J.; Feaster, J. E.; Harlow, R. L. *Organometallics* **1990**, *9,* 2653−2655.
(9) Burk, M. J.; Gross, M. F.; Harper, T. G. P.; Kalberg, C. S.; Lee, J. R.; Martinez, J. P. *Pure Appl. Chem.* **1996**, *68,* 37−44.
(10) Saburi, M.; Ohnuki, M.; Ogasawara, M.; Takahashi, T.; Uchida, Y. *Tetrahedron Lett.* **1992**, *33,* 5783−5786.
(11) Ashby, M. T.; Khan, M. A.; Halpern, J. *Organometallics* **1991**, *10,* 2011−2015.
(12) Chan, A. S.; Laneman, S. A.; Day, C. X. *Inorg. Chim. Acta* **1995**, *228,* 159−163.
(13) Mashima, K.; Kusano, K.; Sato, N.; Matsumura, Y.; Nozaki, K.; Kumobayashi, H.; Sayo, N.; Hori, Y.; Ishizaki, T.; Akutagawa, S.; Takaya, H. *J. Org. Chem.* **1994**, *59,* 3064−3076.
(14) Kawano, H.; Ishii, Y.; Kodama, T.; Saburi, M.; Uchida, Y. *Chem. Lett.* **1987**, 1311−1314.
(15) A search of the Cambridge Structural Database (April 1996 Edition) revealed no Ru−DuPHOS structures.

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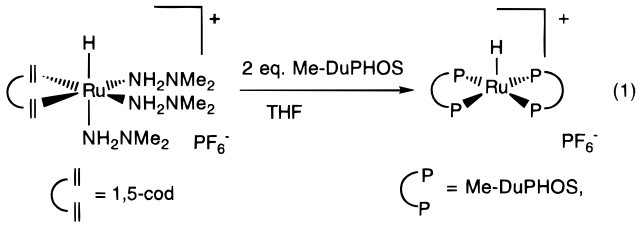
the catalyst precursor in a series of enantioselective hydrogenations.[10,16,17] In solution it loses one of the BINAP ligands to form the catalytically active species. Complex **1** readily reacts with H_2(g) to form the chiral dihydrogen complex *trans*-[Ru(η^2-H_2)H(BINAP)$_2$]PF_6 **(2)**. Both complexes have been characterized by NMR, but no X-ray structural data were obtained. The dihydrogen complex **2** is analogous to a series of complexes *trans*-[M(η^2-H_2)H(P-P)$_2$]$^+$ (M = Fe, Ru, Os; P-P = nonchiral chelating diphosphine ligand) investigated in detail by our group.[18−27] We here present the synthesis, properties, and X-ray crystal structure of the complex *trans*-[Ru(η^2-H_2)H(R,R′-Me-DuPHOS)$_2$]PF_6 **(4)**, which incidentally is also the first X-ray structure determination of a ruthenium complex with an η^2-H_2 trans to a hydride ligand. **4** is potentially useful as a well-defined catalyst precursor for hydrogenation reactions with the ruthenium DuPHOS system.

Results and Discussion

Preparation and NMR Spectroscopy. The synthesis of the 5-coordinate complex [RuH(DuPHOS-Me)$_2$]-PF_6 **(3)** and the corresponding dihydrogen complex *trans*-[Ru(η^2-H_2)H(R,R′-Me-DuPHOS)$_2$]PF_6 **(4)** was carried out in analogy to the preparation of complexes **1** and **2** reported by Tsukahara et al.[17] The complex [RuH(NH$_2$NMe$_2$)$_3$(cod)]PF_6, cod = cyclooctadiene, a synthon for a [RuH$^+$] fragment,[28,29] reacts instantaneously with 2 equiv of R,R′-Me-DuPHOS in boiling THF or more slowly at room temperature to give the deep red complex **3**, which can be isolated in >80% yield by precipitation of the complex by use of diethyl ether under Ar (eq 1). Attempts at crystallization of **3** under N_2 at −30 °C produced instead crystals of the thermally unstable dinitrogen complex *trans*-[Ru(N_2)H(R,R′-Me-DuPHOS)$_2$]PF_6 **(5)** (see below).



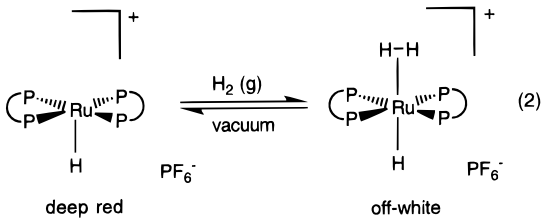
(1)

The ^{1}H NMR spectrum of the monohydride complex **3** in CD_2Cl_2 or THF-d_8 at 298 K under Ar shows a broad quintet at −32.8 ppm with ^2J(H,P) = 21 Hz as the only resonance in the hydride region. The fact that the chemical shift is the same in the two solvents suggests that complex **3** does not coordinate solvent. Complex **3** is crystallized from THF, but its spectrum in CD_2Cl_2 contains only tiny resonances for free THF, much less than the 1 equiv expected if the THF were coordinated upon precipitation of **3**. Therefore THF is not coordinated. When excess water is added to **3** in CD_2Cl_2, there is no change in the hydride region of the ^{1}H NMR spectrum. It seems that water also does not coordinate to **3**. The ^{31}P{^{1}H} NMR spectrum of **3** in CD_2Cl_2 shows two broad signals of equal intensity at 85.8 and 83.0 ppm and the heptet pattern of free PF_6^-. The heptet does not change at low temperature. Therefore, the PF_6^- anion is not coordinated. In view of the rigid structure of the DuPHOS ligand (see Figure 1), the coordination to the ruthenium of a carbon−hydrogen bond from the ligand appears to be unlikely and we have found no spectroscopic evidence for an agostic C−H bond.

The ^{1}H NMR spectrum suggests a distorted square-based pyramidal structure for the complex in solution, in which the hydride ligand occupies the apical position. This geometry is expected for 5-coordinate complexes that do not have π-donor ligands.[23,30−32] In contrast the analogous five-coordinate BINAP complex **1** has been reported to form a 2:1 mixture of isomers in $CDCl_3$ solution. The geometry of the major isomer is believed to be analogous to **3**, while in the minor isomer the hydride ligand is thought to occupy a basal position in the distorted pyramid, cis to the free coordination site.[17]

Reaction of a solution of **3** with H_2(g) produces a light-yellow, air-sensitive solution of the dihydrogen complex **4**, which can be isolated in >80% yield as an off-white microcrystalline solid. The presence of 1,1-dimethylhydrazine does not interfere with the formation of the complex, presumably because the hydrazine is too large to fit as a ligand into the sterically encumbered dihydrogen binding site. Under an atmosphere of H_2(g) at 298 K the complex is stable in solution for several days but starts to decompose over extended periods of time. Substituting H_2(g) with D_2(g) gas leads to the formation of a mixture of isotopomeric complexes containing [Ru(η^2-HD)H(DuPHOS-Me)$_2$]PF_6 **(4a)** and [Ru(η^2-HD)D-(DuPHOS-Me)$_2$]PF_6 **(4b)**. The dihydrogen ligand in **4** is only loosely bound. Exposing a solid sample of the dihydrogen complex **4** to vacuum for several seconds results in a distinct color change to red, the color of the 5-coordinate complex **3**. Introduction of H_2(g) quantitatively regenerates the off-white dihydrogen complex (eq 2). This process is completely reversible for at least 10 cycles as indicated by a subsequent ^{1}H NMR spectrum of the sample.

(16) Saburi, M.; Takeuchi, H.; Ogasawara, M. T.; Tsukahara, Y. I.; Ikariya, T.; Takahashi, T. *J. Organomet. Chem.* **1992**, *428*, 155−167 and references therein.
(17) Tsukahara, T.; Kawano, H.; Ishii, Y.; Takahashi, T.; Saburi, M.; Uchida, Y.; Akutagawa, S. *Chem. Lett.* **1988**, 2055−2058.
(18) Morris, R. H. *Can J. Chem.* **1996**, in press.
(19) (a) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *188*, 5396−5407. (b) Morris, R. H.; Wittebort, R. *Magn. Reson. Chem.*, in press.
(20) Schlaf, M.; Maltby, P. A.; Lough, A. J.; Morris, R. H. *Organometallics* **1996**, *15*, 2270−2278 and references therein.
(21) Cappellani, E. P.; Drouin, S. D.; Jia, G.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *J. Am. Chem. Soc.* **1994**, *116*, 3375−3388.
(22) Morris, R. H.; Schlaf, M. *Inorg. Chem.* **1994**, *33*, 1725−1726; correction 5366.
(23) Chin, B.; Lough, A. J.; Morris, R. H.; Schweitzer, C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278−6288.
(24) Farrar, D. H.; Maltby, P. A.; Morris, R. H. *Acta Crystallogr.* **1992**, *C48*, 28−31.
(25) Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027−3039.
(26) Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876−4887.
(27) Baustista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7031−7036.
(28) Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1976**, 705−706.
(29) Ashworth, T. A.; Singleton, E.; Hough, J. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1809−1815.
(30) Thorn, D. L.; Hoffmann, R. *New. J. Chem.* **1979**, *3*, 39−45.
(31) Rachidi, I. E.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671−677.
(32) Lough, A. J.; Morris, R. H.; Schlaf, M. *Acta Crystallogr. C* **1996**, in press.



The ^{1}H NMR spectrum of the dihydrogen complex **4** in CD_2Cl_2 at 298 K shows two broad singlets at −5.78 and −9.50 ppm for the η^2-H_2 and terminal hydride ligand in the expected 2:1 ratio of integrals. The resonances of the η^2-HD ligand in the mixture of the isotopomeric complexes **4a**,**b** appear as two overlapping 1:1:1 triplets at −5.77 and −5.84 ppm, respectively, with a J(H,D) coupling constant of 30 Hz. Above 213 K there is proton exchange between the two ligands leading to the observed broadening of the terminal hydride signal and formation of the isotopomers **4a/b**. Below 213 K the signal of the terminal hydride in **4** resolves into an overlapping triplet of triplets with coupling constants of ^2J(H,P) = 25 and 17 Hz.

In general complexes of the type *trans*-[MH(X^{z-})(P-P)$_2$]$^{+(1-z)}$, (X = H^-, Cl^-, Br^-, η^2-H_2) show a binomial quintet in the ^{1}H NMR spectra for the terminal hydride ligand and a singlet in the ^{31}P NMR spectra indicating equivalent ^{31}P nuclei. In these complexes this must be a consequence of some torsional flexibility of the ligand backbone leading to a time-averaged solution structure with phosphorus environments which are equivalent. Regardless of any motion of the ligands, the chirality of complex **4** limits its symmetry to C_2 as shown in Figure 2, which renders the phosphorus nuclei pairwise chemically and magnetically inequivalent, resulting in coupling patterns that are normally observed for *cis*-diphosphine complexes. With a postulated C_2 symmetry of the complex **4** in solution an AXX′YY′ spin system is expected for the hydride ligand.[33] The simplification ^2J(H,P_x) = ^2J(H,$P_{x'}$) and ^2J(H,P_y) = ^2J(H,$P_{y'}$) leads to the observed coupling pattern, which corresponds to an AX_2Y_2 spin system resulting in a pseudo-first-order spectrum. The 4 phosphorus nuclei form the subsystem XX′YY′, which with ^2J(P_x,P_y) = ^2J(P_x,$P_{y'}$), also effectively becomes an X_2Y_2 spin system. This is in agreement with the observed ^{31}P{^{1}H} NMR, which shows a pseudo-first-order spectrum consisting of two triplets at 86.0 and 89.5 ppm when the solvent is CH_2Cl_2 with a coupling value of ^2J(P_x,P_y) = ^2J(P_x,$P_{y'}$) = 20 Hz. In EtOH or THF (reaction mixtures) they are shifted upfield by ∼1.5 ppm. The ^{31}P NMR coupling patterns are equivalent to those observed for the complex *trans*-RuHCl(4*R*, 5*R*-diop)$_2$ reported by Ball et al.[34]

The H−H distance of **4** in solution can be estimated on the basis of the J(H,D) value of the HD complex **4a** and the T_1(min) value of the dihydrogen ligand.[19] An empirical correlation[19] between d(HH) and J(H,D) provides an H−H distance of 0.92 Å when J(H,D) = 30 Hz. The T_1(min) value of the η^2-H_2 is 9.0 ± 0.5 ms at 216 ± 2 K, at 216 ± 2 K, 400 MHz, (Table 1). From the X-ray structure determination (*vide infra*) the closest contact of the protons of the η^2-H_2 ligand with other

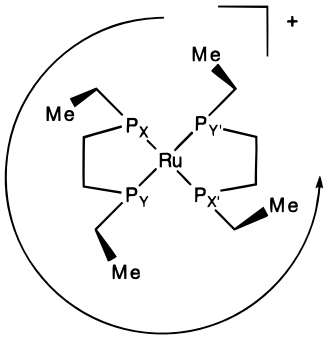


Figure 2. Schematic drawing of the structure of **4** viewed down its C_2 axis along the ruthenium−hydride bond vector illustrating the helixlike topology of the complex. The labels on the phosphorus atoms relate to the XX′YY′ spin system imposed by the C_2 symmetry.

Table 1. Observed and Calculated T_1 Values of the Dihydrogen Ligand in *trans*-[Ru(η^2-H_2)H(DuPHOS-Me)$_2$]PF_6 in CD_2Cl_2 solution at 400 MHz

	T_1 (ms)			T_1 (ms)	
T (K)	obsd	calcd[a]	T (K)	obsd	calcd[a]
293	36.1[b]	27.0	208	9.8	9.9
272	17.1	18.8	186	14.7	15.6
251	12.3	13.0	176	24.6	23.5
229	9.9	9.9			

[a] Calculated by use of a computer program fitting the T_1 data to the T_1 equation with a temperature-dependent correlation time $\tau = \tau_o e^{E_a/RT}$; E_a = 2.95 kcal/mol, τ_o = 2.73 ps, and d_{HH} = 0.99 Å.[26] [b] The T_1 value of the hydride resonance is 74 ms at 293 K. Therefore because of site exchange with the hydride the T_1 value of the H_2 ligand is greater than the one calculated and the T_1 value of the hydride is shorter than expected (approximately 200 ms expected).

NMR active nuclei occurs with those of the methyl hydrogens on the chiral ring carbons with distances ranging from 2.03 to 2.79 Å. If one corrects for the relaxation contributions from these protons as well as those from the four ^{31}P nuclei, the effective T_1(min) value is 10 ms corresponding to the two possible H−H distances of 0.78 Å for a fast-spinning η^2-H_2 ligand and 0.99 Å for a slow spinning one.[19,27,35,36] The latter value is in better agreement with the value of 0.92 Å from J(H,D). Complex **4** with its slow-spinning H_2 ligand is in contrast to the related complexes *trans*-[Ru(η^2-H_2)H($R_2PCH_2CH_2PR_2$)$_2$]$^+$ (R = Et, Ph), which probably have fast-spinning η^2-H_2 ligands.[23,27] For a fast-spinning H_2 ligand it may be necessary to have the planar MP_4 core which these last mentioned complexes can easily adopt; the nonplanar RuP_4 core in the crowded molecule **4** is held rigidly in place by interligand interactions (see the discussion of the solid state structure of **4**, below). A torsional libration of the dihydrogen ligand over the P(2)−Ru−P(4) axis through a root-mean-square angle of 20° would explain why the no-motion T_1 calculation provides a longer distance than the J(H,D) method.[19b] The experimental T_1 data closely match, with the exception of the value at room temperature, those calculated from the temperature-dependent T_1 equation. The discrepancy at room temperature is accounted for by exchange of H atoms between the

(33) Hesse, M.; Meier, H.; Zeh, B. *Spektroskopische Methoden in der Organischen Chemie*; Georg Thieme Verlag: Stuttgart, Germany, 1987.
(34) Ball, R. G.; James, B. R.; Trotter, J.; Wang, D. K. W. *J. Chem. Soc., Chem. Commun.* **1979**, 460−461.
(35) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126−4133.
(36) Desrosier, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173−4184.

dihydrogen and hydride sites which becomes important at ≥293 K. This also explains why the T_1 of the terminal hydride is very small (74 ms, 400 MHz) at 293 K because of relaxation averaging with the dihydrogen nuclei. Below 293 K the hydride resonance is a sharp quintet associated with a long T_1, but exact values were not determined. The complex has an unusually high activation energy of $E_a = 2.95$ kcal/mol for reorientation in solution.

The deprotonation of **4** with a strong base such as *n*-BuLi in THF solution leads to the formation of the highly air-sensitive, orange dihydride complex RuH_2-(DuPHOS-Me)$_2$ **(6)**. The ^{1}H NMR spectrum at 298 K in CD_2Cl_2 shows a second-order, equally spaced septet of nonbinomial intensities at −10.45 ppm with ^2J(H,P) = 25 Hz. In an impure sample where **4** and **6** were present, proton exchange between these complexes was slow on the NMR time scale because the resonances for both species were well-resolved. This may be a consequence of the high steric demand of the chelating phosphine ligand that prevents a close enough approach of the two complexes to allow direct proton exchange in the absence of a smaller, mediating base. The ^{31}P{^{1}H} of **6** in THF at 298 K shows two triplets (XX′YY′ spin system) at 99.7 and 102.6 ppm with a coupling constant $^2J(P_x,P_y) = {}^2J(P_x,P_{y'}) = 19$ Hz along with some free ligand at 2.68 ppm, indicating some decomposition of the dihydride complex at 298 K. Tsukahara et al. also reported the formation of the analogous complex RuH_2(BINAP)$_2$ but did not publish structural or spectroscopic information.[17]

The stereochemistry of the dihydride complex **6** can be determined on the basis of the ^{31}P NMR data. A molecular model showed that a *trans*-dihydride complex would have D_2 symmetry with one C_2 axis along the H−Ru−H bond vector and two C_2 axes bisecting the angles P−Ru−P. In this point group all four phosphorus nuclei are chemically equivalent resulting in a X_4 spin system. This is not in agreement with the observed ^{31}P{^{1}H} NMR spectrum. Distorting the complex by twisting the chelating phosphines against each other, as observed in the X-ray structure of the C_2 complex **4**, does not break the D_2 symmetry. A *cis*-dihydride complex on the other hand would keep the C_2 symmetry of complex **4** with the C_2 axis perpendicular to the axial phosphorus nuclei and bisecting the angle H−Ru−H. In this case the XX′YY′ spin system would be maintained. We therefore propose that in spite of severe steric constraints **6** adopts a cis geometry in order to avoid the energetically unfavorable trans positioning of the two hydride ligands. A plastic model of the cis complex showed that this appears to be possible, if the complex adopts Λ helicity.[37] Because of the near planarity of the individual chelates the formation of λ or δ isomers is not expected.

The dinitrogen complex **5** as prepared above was dissolved in CD_2Cl_2 under 1 atm of N_2 and examined by variable-temperature ^{31}P{^{1}H} and ^{1}H NMR. At −40 °C or below the ^{31}P NMR spectrum contained two sharp triplets of an A_2X_2 spin system at 78.7 and 70.4 ppm due to **5** and a small amount (approximately 5%) of two multiplets due to **3**. There were also small resonances due to **4**, probably formed from the reaction of **3** with traces of H_2 in the glovebox N_2 atmosphere. The ^{1}H NMR spectrum had resonances for all of these species, the major one in the hydride region being a quintet at −14.98 ppm for **5**. The ^{31}P NMR spectrum at room temperature had two major broad resonances at 79.4 and 72.4 ppm suggesting an averaging of resonances due to **5** and **3** exchanging according to eq 3 at a rate of

$$[Ru(N_2)(H)(DuPHOS\text{-}Me)_2]^+ \rightleftarrows [Ru(H)(DuPHOS\text{-}Me)_2]^+ + N_2 \quad (3)$$

about 10^3 Hz. The small dihydrogen resonances were sharp and not participating in an exchange process. Therefore, the dihydrogen ligand is less labile than the dinitrogen ligand at room temperature.

The dinitrogen stretching absorption at 2184 cm^{-1} for **5** indicates that the [RuH(DuPHOS-Me)$_2$]$^+$ moiety is a weak π-back-bonder. This is consistent with the fact that both the dinitrogen and dihydrogen complexes are very labile.[19]

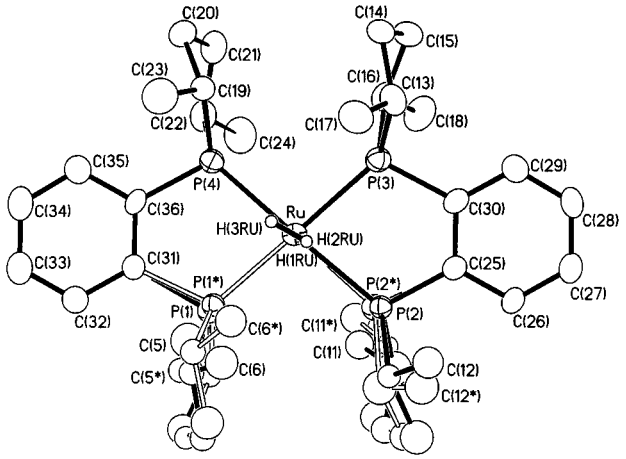


Figure 3. ORTEP drawing of the structure of *trans*-[Ru(η^2-H$_2$)H(DuPHOS-Me)$_2$]$^+$ (**4**) at 50% probability level. The PF_6^- counterion is not shown.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in 4

Ru−H(1Ru)	1.93(9)	Ru−P(4)	2.346(4)
Ru−H(2Ru)	1.78(7)	P(1)−C(31)	1.83(2)
Ru−H(3Ru)	1.78(7)	P(1*)−C(31)	1.87(2)
H(2Ru)−H(3Ru)	0.8(2)	C(31)−C(36)	1.38(2)
Ru−P(1)	2.393(14)	C(36)−P(4)	1.811(12)
Ru−P(1*)	2.259(13)	P(2)−C(25)	1.75(2)
Ru−P(2)	2.372(12)	P(2*)−C(25)	1.89(2)
Ru−P(2*)	2.307(13)	C(25)−C(30)	1.40(2)
Ru−P(3)	2.350(4)	C(30)−P(3)	1.835(12)

H(3Ru)−Ru−H(2Ru)	26(6)	P(1)−Ru−P(3)	169.4(3)
H(2Ru)−Ru−H(1Ru)	173(6)	P(1*)−Ru−P(3)	164.0(3)
H(3Ru)−Ru−H(1Ru)	161(6)	P(2)−Ru−P(4)	175.0(3)
P(1)−Ru−P(4)	83.4(3)	P(2*)−Ru−P(4)	169.1(4)
P(1*)−Ru−P(4)	82.8(3)	Ru−P(1)−C(31)	108.2(7)
P(2)−Ru−P(3)	81.3(3)	Ru−P(1*)−C(31)	112.7(7)
P(2*)−Ru−P(3)	84.3(4)	Ru−P(4)−C(36)	110.0(4)
P(1)−Ru−P(2)	98.5(4)	Ru−P(2)−C(25)	112.0(7)
P(1*)−Ru−P(2*)	98.2(5)	Ru−P(2*)−C(25)	109.5(7)
P(3)−Ru−P(4)	97.71(12)	Ru−P(3)−C(30)	110.6(4)

Solid-State Structure of the Dihydrogen Complex 4. An ORTEP drawing of the structure of the cation of **4** is shown in Figure 3. The PF_6^- counterion is not shown. The closest contact with the PF_6^- counterion occurs at 2.429 Å with a hydrogen atom of the methyl group C(24). Selected bond lengths and angles are listed in Table 2. The ruthenium atom in the

(37) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Holt-Saunders: Philadelphia, London, Tokyo, 1977.

complex is coordinated in a distorted octahedral environment by the two chelating R,R′-Me-DuPHOS ligands. With $Z = 4$ the complex does not occupy a special position in the unit cell but has C_2 symmetry within the 4σ level of bond lengths and angles. The symmetry axis is aligned along the ruthenium−hydride bond vector. Due to the orientation of the methyl groups on the chiral centers the complex has a helixlike topology as illustrated in Figure 2. The η^2-H_2 as well as the hydride ligand are therefore located in a *chiral pocket* on either side of the main plane of the complex. The phosphorus atoms P(2) and P(3) and the attached carbon rings are disordered over two sites. The disorder was successfully modeled with 50:50 occupancy. The two planes defined by the ruthenium atom and the chelates P(1)−C(31)−C(36)−P(4) and P(2)−C(25)−C(30)−P(3) or the corresponding planes containing the chelates P(1*)−P(4) and P(2*)−P(3) are almost perfectly planar and twisted against each other by an angle of 12.3 or 20.4°, respectively. This twist angle is a consequence of the steric requirements of the methyl groups on the eight stereocenters C(1), C(4), C(7), C(10), C(13), C(16), C(19), and C(22) that force the phosphorus atoms out of the ideal square planar arrangement around the metal, resulting in the observed distortion, which has no influence on the approximate C_2 symmetry. The chelate angles of the phosphines vary from 81.3(3) to 84.3(3)°. The Ru−P bond lengths vary from 2.346(4) to 2.393(14) Å, which positions them closer to the upper limit of observed Ru−P bond distances.[38] This is another consequence of the high steric demand of the chelate and has also been reported for the BINAP complex RuHCl(BINAP)$_2$, which has Ru−P bond lengths of 2.373(4)−2.420(4) Å.[14] The bond lengths of the two disordered phosphorus atoms P(1*) and P(2*), 2.307 and 2.259 Å, respectively, are significantly shorter. Possibly the larger twist angle of the two phosphine chelates in the disordered position further relieves steric constraints between the phospholane backbones and hence allows for a closer ruthenium phosphorus interaction. The hydrogen atoms of the η^2-H_2 ligand and the trans hydride ligand were located in an electron density Fourier difference map, and their positions, isotropically refined. From this refinement the η^2-H_2 ligand is found to be aligned in an almost eclipsed position along the P(2)−Ru−P(4) unit which is bent away from the H_2 ligand with an angle of 175.0(3)°. This alignment may be favored because it optimizes π-back-bonding from the filled d_{yz} or d_{xz} orbital of the d^6-metal center into the σ^* orbital of the η^2-H_2 ligand.[20] The P(1)−Ru−P(3) angle of 169.4(3)° is bent toward the H_2 ligand. The H−H distance from the isotropic refinement is 0.8(2) Å, consistent with either a slow- or fast-spinning η^2-H_2 ligand. The high esd and the disorder in the crystal make a quantitative interpretation of this value impossible.

Crystal Structure of the Dinitrogen Complex 5. The dinitrogen complex **5** (Figure 4) has a similar but even more crowded coordination sphere than complex **4**. A difference is that both the P(2)−Ru−P(4) angle of 164.17(6)° and the P(1)−Ru−P(3) angle of 175.65(6)° are bent away from the N_2 ligand. As in the dihydrogen complex, the twisting of the two ligands is dictated by interligand contacts. Also found to be disordered in the crystal was a minor component, possibly square-pyramidal complex **3**, formed by loss of N_2 from **5**. This species refined with three long Ru−P bonds (2.36−2.38 Å) and one shorter bond (2.288(5) Å).

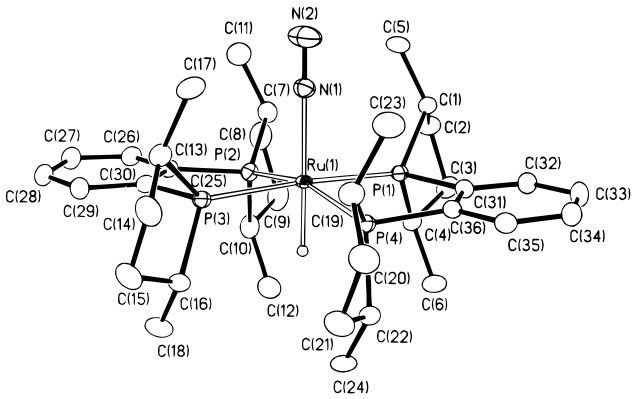


Figure 4. ORTEP drawing of the structure of *trans*-[Ru(N_2)H(DuPHOS-Me)$_2$]$^+$ (**5**) at 50% probability level. The PF_6^- counterion is not shown.

Table 3. Bond Lengths (Å) and Angles (deg) for 5

Ru(1)−H(1RU)	1.57(8)	Ru(1)−N(1)	2.046(3)
Ru(1)−P(4)	2.3483(7)	Ru(1)−P(2)	2.3488(8)
Ru(1)−P(3)	2.3594(8)	Ru(1)−P(1)	2.3604(8)
P(1)−C(31)	1.837(3)	P(1)−C(4)	1.859(3)
P(1)−C(1)	1.880(3)	P(2)−C(10)	1.876(3)
P(2)−C(25)	1.831(3)	P(2)−C(7)	1.857(3)
P(3)−C(30)	1.838(3)	P(3)−C(16)	1.856(3)
P(3)−C(13)	1.883(3)	P(4)−C(22)	1.880(3)
P(4)−C(36)	1.840(3)	P(4)−C(19)	1.861(3)
N(1)−N(2)	1.090(4)		
P(1)−Ru(1*)	2.369(6)	P(2)−Ru(1*)	2.288(5)
P(3)−Ru(1*)	2.376(6)	P(4)−Ru(1*)	2.364(5)
H(1RU)−Ru(1)−N(1)	179(2)	H(1RU)−Ru(1)−P(4)	83(2)
N(1)−Ru(1)−P(4)	97.66(8)	H(1RU)−Ru(1)−P(2)	81(2)
N(1)−Ru(1)−P(2)	98.16(8)	P(4)−Ru(1)−P(2)	164.17(6)
H(1RU)−Ru(1)−P(3)	87(2)	N(1)−Ru(1)−P(3)	92.31(8)
P(4)−Ru(1)−P(3)	96.90(3)	P(2)−Ru(1)−P(3)	83.04(3)
H(1RU)−Ru(1)−P(1)	89(2)	N(1)−Ru(1)−P(1)	91.98(8)
P(4)−Ru(1)−P(1)	83.28(3)	P(2)−Ru(1)−P(1)	95.59(3)
P(3)−Ru(1)−P(1)	175.65(6)	N(2)−N(1)−Ru(1)	178.5(3)
C(31)−P(1)−C(4)	105.42(13)	C(1)−P(1)−Ru(1)	126.28(10)
C(31)−P(1)−C(1)	101.08(13)	C(4)−P(1)−C(1)	93.50(13)
C(31)−P(1)−Ru(1)	109.58(9)	C(4)−P(1)−Ru(1)	118.03(10)
C(7)−P(2)−C(10)	93.57(14)	C(7)−P(2)−Ru(1)	219.16(10)
C(25)−P(2)−C(7)	107.30(13)	C(25)−P(2)−C(10)	99.14(14)
C(25)−P(2)−Ru(1)	110.05(8)	C(10)−P(2)−Ru(1)	124.71(11)
C(30)−P(3)−C(16)	104.49(14)	C(13)−P(3)−Ru(1)	126.34(10)
C(30)−P(3)−C(13)	100.90(13)	C(16)−P(3)−C(13)	93.09(13)
C(30)−P(3)−Ru(1)	109.72(9)	C(16)−P(3)−Ru(1)	118.99(10)
C(36)−P(4)−C(19)	106.20(13)	C(36)−P(4)−C(22)	99.73(13)
C(22)−P(4)−Ru(1)	125.39(10)	C(36)−P(4)−Ru(1)	109.73(9)
P(2)−Ru(1*)−P(4)	178.8(6)	P(2)−Ru(1*)−P(1)	97.0(2)
P(4)−Ru(1*)−P(1)	82.8(2)	P(2)−Ru(1*)−P(3)	84.0(2)
P(4)−Ru(1*)−P(3)	96.0(2)	P(1)−Ru(1*)−P(3)	167.4(5)

Experimental Section

Oxygen and water were excluded at all times by the use of a glovebox supplied with purified nitrogen or vacuum lines supplied with purified N_2 or Ar. Et_2O was predried over KOH and distilled from sodium−benzophenone ketyl. CH_2Cl_2 was distilled from calcium hydride. Ethanol and methanol were distilled from Mg activated with I_2. Toluene was distilled from sodium. CD_2Cl_2 was dried over Linde type 4 Å molecular sieves and degassed prior to use. The complex [RuH(NH_2-NMe_2)$_3$(cod)]PF_6, cod = 1,5-cyclooctadiene, was prepared as reported in the literature.[28,29] NMR spectra were recorded on Varian Unity 400 (400 MHz for ^{1}H, 162 MHz for ^{31}P), Varian

(38) Orpen, A. G.; Bramer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.

Gemini 300 (300 MHz for ^{1}H, 120.5 MHz for ^{31}P), or Varian Gemini 200 (200 MHz for ^{1}H) spectrometers. All ^{31}P NMR spectra were recorded with proton decoupling. ^{31}P NMR chemical shifts were measured relative to ~1% $P(OMe)_3$ in C_6D_6 sealed in coaxial capillaries and are reported relative to H_3PO_4 by use of $\delta(P(OMe)_3) = 140.4$ ppm. ^{1}H chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. In all cases, high-frequency shifts are reported as positive. Variable-temperature T_1 measurements were made at 300 or 400 MHz using the inversion recovery method with calibration of the 90°/180° pulse at each temperature. The temperature of the probes was calibrated with the temperature dependence of the chemical shifts of MeOH.[39] In the X-ray crystal structure determination all calculations were performed and diagrams created using SHELXTL PC on a 486-66 personal computer.[40] FAB-MS measurements were performed in a NBA matrix.

[RuH(DuPHOS-Me)$_2$]PF$_6$ (3). Method 1. R,R′-Me-DuPHOS (200 mg, 0.653 mmol) was dissolved in 20 mL of THF and heated to reflux under Ar. A solution of [RuH(NH_2NMe_2)$_3$-(cod)]PF_6 (200 mg, 0.373 mmol) in 25 mL of THF was added dropwise with stirring to this boiling solution. The reaction mixture turned deep red. The solution was evaporated to dryness in vacuo and the residue recrystallized from THF/Et_2O. Yield: 81% (230 mg, 0.267 mmol) with respect to the Me-DuPHOS added.

Method 2. Similar results are obtained if ethanol is used in place of THF in the preparation.

Method 3. The ligand and starting complex are mixed as above at room temperature and stirred under N_2 for 12 h to provide **3** in a similar yield if the recrystallization is done at 20 °C. If the recrystallization is done at −30 °C, then the dinitrogen complex is obtained (see below). ^{1}H NMR (CD_2Cl_2, 200 MHz), δ: −32.8 (br qnt, J(H,P) 21 Hz, 1 H, RuH), 0.80 (br dd, 6 H, CH_3), 0.91 (br dd, 6 H, CH_3), 1.02 (br, 12 H, CH_3), 1.3−3.4 (m, br, 24 H, CH_2, CH), 7.84, 7.97, and 9.58 (br, 8H phenyl). ^{31}P NMR (120.5 MHz, CD_2Cl_2), δ: 83.0 (br), 85.8 (br). FAB MS: Calcd for $^{12}C_{36}{}^1H_{57}{}^{31}P_4{}^{102}Ru$, 715; m/z obsd M^+, 715.

***trans*-[Ru(N$_2$)H(DuPHOS-Me)$_2$]PF$_6$ (5).** White crystals of the dinitrogen complex were prepared by diffusion of Et_2O into a CH_2Cl_2 solution of complex **3** under N_2 at −30 °C. The white crystals turn red at room temperature due to partial loss of dinitrogen. However the elemental analysis is acceptable for the dinitrogen complex formulation. A pink crystal was also examined by X-ray diffraction (see below). ^{1}H NMR (CD_2Cl_2, 300 MHz, 213 K), δ: −14.98 (qnt, J(H,H) = 18.7 Hz, 1 H, RuH), 0.6 (br, 6 H, CH_3), 0.9 (br, 6 H, CH_3), 1.3 (br, 6 H, CH_3), 2.3 (br, 6 H, CH_3), 1.0−3.5 (m, br, 24 H, CH, CH_2), 7.6−8.0 (br, 8 H, aromatic CH). ^{31}P NMR (120.5 MHz, CD_2Cl_2, 233 K), δ: 78.7 (t, J(P,P) 20.8 Hz), 70.4 (t, J(P,P) 20.8 Hz). IR (Nujol) 2184 cm^{-1} (ν(NN)). Calcd: C, 48.7; H, 6.47; N, 3.15. Found: C, 48.25; H, 6.74; N, 2.75.

***trans*-[Ru(η^2-H$_2$)H(DuPHOS-Me)$_2$]PF$_6$ (4).** The dihydrogen complex was obtained by introducing H_2(g) into the deep-red THF solution of [RuH(DuPHOS-Me)$_2$]PF_6 **(4)**. The reaction mixture can be used directly without isolation of the 5-coordinate intermediate. Bubbling H_2(g) through the deep-red solution of **1** caused a distinct color change to colorless or light yellow within 30 s. The reaction is quantitative as indicated by NMR. Precipitation with Et_2O, filtration, and drying in a stream of H_2(g) gave the complex as an off-white solid in 80% yield (240 mg, 0.28 mmol) with respect to the phosphine ligand and the same amount of starting materials as in the synthesis of **3** above. ^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K), δ: −9.5 (br, 1H, Ru(η^2-H$_2$)*H*), −5.78 (br, 2H, Ru(η^2-*H*$_2$)H), 0.71 (pseudo dd, 3H, CH_3), 1.04 (pseudo dd, 3H, CH_3), 1.13 (pseudo dd, 3H, CH_3), 1.21 (pseudo dd, 3H, CH_3), 1.25−2.8 (br, m, 24H, phospholane backbone), 7.53 (pseudo qnt, J(H,H) = 7.3 Hz, 2H, phenyl), 7.69 (d, J(H,H) = 6.4 Hz, 1H, phenyl), 7.78 (d, J(H,H) = 6.8 Hz, 1H, phenyl). At 193 K the terminal hydride signal is resolved to an overlapping triplet of triplets: −9.74 (tt, J(H,P) = 25, 17 Hz, 1H). ^{31}P NMR (120.5 MHz, CD_2Cl_2), δ: 86.0 (pseudo t, J(P,P) = 21 Hz), 89.5 (pseudo t, J(P,P) = 21 Hz). ^{31}P NMR (120.5 MHz, THF), δ: 84.6, 88.1. ^{31}P NMR (120.5 MHz, EtOH), δ: 84.5, 88.2. FAB MS: Calcd for $^{12}C_{36}{}^1H_{59}{}^{31}P_4{}^{102}Ru$, m/z 717; obsd $(M - H_2)^+$, 715.

***trans*-[Ru(η^2-HD)H(DuPHOS-Me)$_2$]PF$_6$ (4a) and *trans*-[Ru(η^2-HD)D(DuPHOS-Me)$_2$]PF$_6$ (4b).** The HD complex is obtained as a component of an isotopomeric mixture by substituting H_2(g) for D_2(g) in the preparation of **4**. The η^2-HD isotopomers can selectively be observed by nulling out the residual η^2-H_2 signal by an inversion recovery sequence at 213 K using its known T_1 of 9 ms at that temperature. ^{1}H NMR (CD_2Cl_2, 213 K), δ: overlapping 1:1:1 triplets, −5.77 (J(H,D) = 30 Hz, Ru(η^2-HD)D), −5.84 (J(H,D) = 30 Hz, Ru(η^2-HD)H). ^{31}P NMR (120.5 MHz, CD_2Cl_2) (overlapping triplets of isotopomers **4a/b**), δ: 85.98, 88.53 and 86.02, 89.60.

RuH$_2$(DuPHOS-Me)$_2$ (6). To a solution of *trans*-[Ru(η^2-H$_2$)H(DuPHOS-Me)$_2$]PF_6 **(4)** (150 mg, 0.17 mmol) in 15 mL of THF is added BuLi (1.5 M solution in hexane, 0.2 mL, 0.3 mmol) using a microliter syringe. The almost colorless solution instantaneously turns yellow. The solution is stirred for 2 min, and 0.5 mL of MeOH is added to quench the excess BuLi. The solvent is removed in vacuo and the yellow residue redissolved in toluene. The solution is filtered to remove the lithium salts formed, and the complex precipitated as an pale yellow solid by addition of excess MeOH. Yield: 65% (80 mg, 0.11 mmol). ^{1}H NMR (C_6D_6, 300 MHz), δ: −10.45 (nonbinomial spt, approximate intensity distribution 1:3:4:3:4:3:1, J(H,P) = 25 Hz), 0.61 (pseudo dd, 12.8 Hz, 6.9 Hz, 6H, CH_3), 0.85 (pseudo dd, 17.1 Hz, 7.1 Hz, 6H, CH_3), 1.30 (pseudo dd, 13.0 Hz, 6.5, 6H, CH_3), 1.64 (pseudo dd, 15.9 Hz, 7.2 Hz, 6H, CH_3), 1.22−3.02 (br, m, 24H, phospholane backbone), 7.45 (pseudo qnt,

Table 4. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters

	compd	
	4	**5**
empirical formula	$C_{36}H_{59}F_6P_5Ru$	$C_{36}H_{57}F_6N_2P_5Ru\cdot 2CH_2Cl_2$
M_r	861.75	1057.61
cryst size, mm	0.45 × 030 × 0.25	0.36 × 0.33 × 0.23
cryst class	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12$
temp, K	293(2)	173(2)
a, Å	11.457(2)	12.261(1)
b, Å	12.179(2)	14.508(2)
c, Å	29.753(6)	26.249(2)
V, A^3	4151.6(13)	4669.2(8)
Z	4	4
D_{calc}, g cm^{-3}	1.379	1.505
μ(Mo Kα), cm^{-1}	6.21	7.90
F(000)	1792	2176
ω scan width, deg	0.67 + 0.73 tan θ	0.63
range q collctd, deg	2.2−25.0	2.67−30.0
abs corr	ΔF method[41]	ΔF method[41]
min and max transm	0.315, 0.342	0.622, 0.959
no. reflcns collcd	4105	8891
indepdt reflcns	4105	8620
R_{int}	0.00	0.020
no. obsd data [$I > 2\sigma(I)$]	2130	7554
R_1 [$I > 2\sigma(I)^a$]	0.0577	0.0319
wR_2 (all data)^a	0.1527	0.0768
weighting a, b	0.0388, 5.242	0.043, 0.000
goodness of fit	1.037	0.982
absolute struct param	0.01(11)	−0.04(2)
params refined	445	570
max density in ΔF map, e/A^3	0.606	0.453

^{a} Definition of R indices: $R_1 = \sum(F_o - F_c)/\sum(F_o)$, w$R_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

(39) Geet, A. v. *Anal. Chem.* **1970**, *42*, 679−680.
(40) Sheldrick, G. M. SHELXTL/PC V5.0, PC program, Siemens Analytical X-ray Instruments, Inc., Karlsruhe, Germany, 1990.

J(H,H) = 3.0 Hz, 2H, phenyl), 7.85(d, J(H,H) = 5.3 Hz, 1H, phenyl), 7.96 (d, J(H,H) = 4.2 Hz, 1H, phenyl). ^{31}P NMR (120.5 MHz, C_6D_6), δ: 99.66 (pseudo t, J(P,P) = 19 Hz), 102.62 (pseudo t, J(P,P) = 19 Hz).

X-ray Crystal Structure Determination of 4 and 5. Crystals of **4** were obtained by slow diffusion of Et_2O into a saturated CH_2Cl_2 solution of the complex. Pink crystals of **5** prepared as described above were coated with epoxy resin immediately after removal from the refrigerated crystallization solution. Bubbles of dinitrogen could be observed to be forming on the surface of the crystal as it was being mounted. A summary of selected crystallographic data is given in Table 4. In what follows the details of the structure determination of **5**, when different, are given in brackets. Data for compound **4** [**5**] were collected on a Enraf-Nonius CAD4 [Siemens P4] diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The intensities of three standard reflections measured every 120 min [97 reflections] showed no decay. The data were corrected for Lorentz and polarization effects and for absorption.[41]

The structures were solved using the SHELXTL \ PC V5.0[40] package and refined by full-matrix least-squares on F^2 using all data (negative intensities included). All non-hydrogen atoms (except for disordered atoms) were refined with anisotropic thermal parameters. Disordered atoms were refined with isotropic thermal parameters. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were included in calculated positions and treated as riding atoms. The H atoms of the dihydrogen and the hydride in **4** [and the hydride atom in **5**] were refined with isotropic thermal parameters. As a result of conformational disorder of the cation in **4**, two of the P atoms and the attached ligands are disordered over two sites with occupancies 50:50 (see Figure 3). The Ru atom in **5** was refined as a disordered atom with Ru1/Ru1* occupancies 0.93/0.07. The position of the minor component could correspond to the position of the Ru atom in a small amount of the 5-coordinate Ru−H compound present in the lattice. A view of compound **5** is shown in Figure 4.

(41) Sheldrick, G. M. SHELXA-90, Program for Absorption Correction, PC program, Universität Göttingen, Germany, Göttingen, 1990.

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Supporting Information Available: Full details of the X-ray crystal structure determination of **4** and **5**, including tables of X-ray data, positional and thermal parameters, and bond distances and angles and figures of ORTEPs and electron density maps (22 pages). Ordering information is given on any current masthead page.

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