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Synthesis and ^{31}P and ^1H NMR Characterization of Two New Chiral Ruthenium Hydrides Containing the *trans*-1,2-Bis((diphenylphosphino)methyl)cyclobutane Ligand (TBPC): *cis*- $\text{H}_2\text{Ru}(\text{TBPC})_2$ and *trans*- $\text{HRuCl}(\text{TBPC})_2$

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Since the pioneering work of James and co-workers on chiral ruthenium complexes,¹ rather little work has been done on asymmetric reactions catalyzed by ruthenium complexes.² This is mainly due to the paucity of chiral bidentate phosphine ruthenium hydrides³ in spite of their potential for asymmetric catalysis. Moreover, the structure in solution of complexes of the type $\text{HRuCl}(\text{P}-\text{P}^*)_2$ ($\text{P}-\text{P}^*$ = chiral bidentate phosphine) can be difficult to assign from ^{31}P and ^1H NMR spectra. For example, the $\text{HRuCl}(\text{diop})_2$ previously reported as a *cis* isomer on the basis of NMR has been shown by X-ray crystallography to have the hydrogen trans to chlorine.⁴ As part of our recent effort to prepare cheap and readily available catalysts for asymmetric hydrogenation of α,β -unsaturated ketones,⁵ we report here the synthesis and the structural characterization of two new chiral hydrides, *cis*- $\text{H}_2\text{Ru}(\text{TBPC})_2$ (1) and *trans*- $\text{HRuCl}(\text{TBPC})_2$ (2) (TBPC = *trans*-1,2-bis((diphenylphosphino)methyl)cyclobutane). The respective *cis* and *trans* geometries were based on NMR data with use of symmetry considerations and partial decoupling. This methodology provides a general and unequivocal criterion for the establishment of the stereochemistry of configurationally fixed molecules.

Experimental Section

All preparations were performed in Schlenk tubes under dried oxygen-free nitrogen or argon. Solvents were distilled from appropriate drying agents and stored under nitrogen. IR spectra were recorded on a Unicam SP 1100 infrared spectrophotometer. ^1H NMR spectra were obtained at 300 MHz, and proton-decoupled ^{31}P NMR spectra were recorded at 121 MHz with a Bruker AM 300 WB spectrometer. Chemical shifts are in parts per million downfield from 85% H_3PO_4 or from Me_4Si (solvent C_6D_6 , room temperature). Elemental analyses were performed by the Service Central d'Analyses (CNRS) at Vernaison, France.

Reagents. The ruthenium source was $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ obtained from Johnson Matthey Ltd. The precursor compound $(\text{RuCl}_2(\text{COD}))_n$ (COD = cyclooctadiene) was prepared by the literature procedure, and the chiral phosphine TBPC was a gift of the Rhône-Poulenc Co.⁶

Preparation of Complex 1. A suspension of $(\text{RuCl}_2(\text{COD}))_n$ ⁷ (100 mg, 0.36 mmol) and *trans*-1,2-bis((diphenylphosphino)methyl)cyclobutane (*R* isomer, $[\alpha]_D^{25} -17.8^\circ$ (*c* 1, C_6H_6); 324 mg, 0.72 mmol) was refluxed in 20 mL of ethanol containing 160 mg (1.60 mmol) of $\text{N}(\text{Et})_3$ under N_2 for 20 h. After the solution was cooled, the yellow solid precipitate was filtered, washed with ethanol, and vacuum-dried: yield 59%; mp 178°C ; $[\alpha]_D^{25} -110^\circ$ (*c* 0.5, benzene). IR (Nujol): ν_{RuH} 1955 and 1910 cm^{-1} . ^1H NMR: Ru-H -9.7 ppm (multiplet). $^{31}\text{P}\{^1\text{H}\}$ NMR: 38.9 (t) and 23.7 ppm (t) ($J_{\text{P-P}} = 15.9$ Hz). Anal. Calcd for $\text{C}_{60}\text{H}_{62}\text{P}_4\text{Ru}$: C, 71.4; H, 6.1; P, 12.3. Found: C, 71.1; H, 5.95; P, 11.9.

Complex 2. The preparative procedure for this complex is the same as that above, but with only 1 equiv of $\text{N}(\text{Et})_3$ (48 mg, 0.47 mmol) instead of excess. The yellow-white powder was filtered, washed with

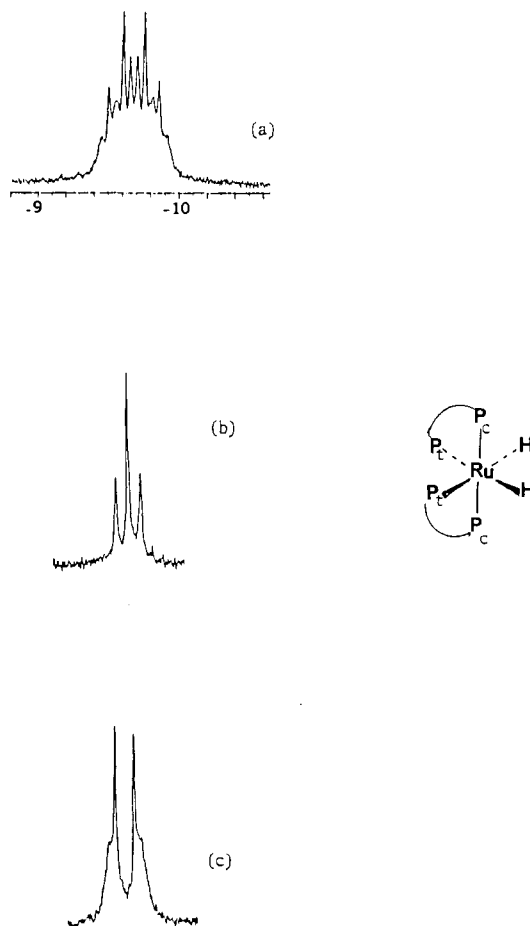


Figure 1. High-field hydride region of the 300-MHz ^1H NMR spectrum of $\text{H}_2\text{Ru}(\text{TBPC})_2$: (a) normal spectrum; (b) spectrum after irradiation of the ^{31}P peak at 38.9 ppm; (c) spectrum after irradiation of the ^{31}P peak at 23.7 ppm.

ethanol, and vacuum-dried: yield 52%; mp 166°C ; $[\alpha]_D^{25} +88^\circ$ (*c* 0.4, benzene). IR (Nujol): $\nu_{\text{Ru-H}}$ 2020 cm^{-1} . ^1H NMR: Ru-H -18.2 ppm (septuplet). $^{31}\text{P}\{^1\text{H}\}$ NMR: 27.9 (t) and 8.2 ppm (t) ($J_{\text{P-P}} = 39.2$ Hz). Anal. Calcd for $\text{C}_{60}\text{H}_{61}\text{ClP}_4\text{Ru}$: Cl, 3.4. Found: Cl, 3.1.

Results and Discussion

The reaction of $(\text{RuCl}_2(\text{COD}))_n$ ⁷ with 2 equiv of optically active *R*-(-)-TBPC⁶ in the presence of an excess of triethylamine (4 equiv) under ethanol reflux conditions yields the yellow complex $\text{H}_2\text{Ru}(\text{TBPC})_2$ (1) in good yield (59%). However, if 1 equiv of

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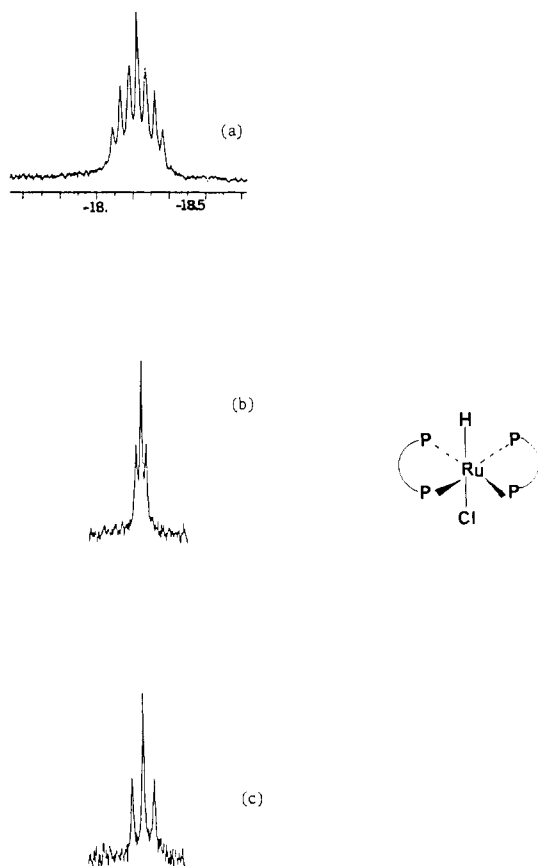


Figure 2. High-field hydride region of the 300-MHz ^1H NMR spectrum of $\text{HRuCl}(\text{TBPC})_2$: (a) normal spectrum; (b) spectrum after irradiation of the ^{31}P peak at 27.9 ppm; (c) spectrum after irradiation of the ^{31}P peak at 8.2 ppm.

triethylamine is added to the solution, only one chlorine atom is removed from the complex precursor and we note the formation of the monohydride $\text{HRuCl}(\text{TBPC})_2$ (**2**). Both syntheses are variations of the synthetic method of Ikariya et al.^{3c} The complexes gave satisfactory elemental analyses, and the configuration (cis or trans) was based on NMR data. Stereochemical assignments of the nonrigid molecules $\text{M}(\text{bidentate phosphine})_2\text{XY}$ must be approached with caution,^{4,8} but with complexes **1** and **2** the cyclobutane ring fixes the configuration of the ruthenium chelate ring.

For the molecule $\text{H}_2\text{Ru}(\text{TBPC})_2$, we can envisage two chiral isomers, the cis isomer with C_2 symmetry or the trans isomer with D_2 symmetry. This differs from the situation with $\text{H}_2\text{Ru}(\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2)_2$,⁹ which, because of the flexibility of the ethylene bridge, gives rise to C_{2v} and D_{2h} symmetry for the cis and trans isomers, respectively. With complex **1**, for the trans isomer, the proton-decoupled ^{31}P NMR spectrum should exhibit a single resonance due to the four equivalent phosphorus nuclei, whereas in the cis isomer the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum will appear as two triplets, one for each pair of cis and trans phosphorus nuclei. The data presented here are in accord with the cis isomer. This result can be unambiguously confirmed by the use of selective ^{31}P -decoupled ^1H NMR spectra. The cis isomer possesses magnetically nonequivalent hydrides because two different coupling constants to the $^{31}\text{P}_i$ atoms are involved. However, irradiation of the trans phosphorus nuclei (P_t , Figure 1) effectively removes this magnetic nonequivalence, leading to a single binomial triplet. In contrast, irradiation of the cis phosphorus nuclei (P_c , Figure 1) maintains their magnetic nonequivalence since each proton still possesses a cis $J_{\text{P-H}}$ and a trans $J_{\text{P-H}}$. Accordingly P_t was irradiated to give spectrum b ($J_{\text{P-H}} = 26.8$ Hz) and P_c to give spectrum c.

Thus the assignment of **1** as the cis isomer is firmly based.

Complex **2** likewise shows two triplet resonances in the ^{31}P spectrum. This, however, is indicative of the formation of the trans isomer (which has C_2 symmetry) rather than the cis molecule (which would be C_1 , and so have four different phosphorus environments). The normal ^1H NMR spectrum shows a 1:2:3:4:3:2:1 septet assignable as an overlapping triplet of triplets where one of the $J_{\text{P-H}}$ values is approximately double that of the other. This has been experimentally verified by selective irradiation of each of the phosphorus environments. Irradiation of the ^{31}P peak at 27.9 ppm gives a 11.8-Hz triplet while the corresponding irradiation at 8.2 ppm produces a proton triplet with $J_{\text{P-H}} = 27$ Hz (see Figure 2). We note that the closely analogous product $\text{HRuCl}(\text{diop})_2$ has been shown crystallographically to be the trans complex.⁴ The spectra reported therein and the data presented here are entirely in accord with the formation of the trans isomer.

To conclude, simple symmetry considerations and the use of selective ^{31}P -decoupled ^1H NMR spectra can be successfully applied to stereochemical determination of rigid chiral complexes $\text{H}_2\text{M}(\text{P-P}^*)_2$ and $\text{HMCl}(\text{P-P}^*)_2$. Utilization of the two compounds in asymmetric catalysis will be reported elsewhere.¹⁰

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Registry No. **1**, 106588-05-0; **2**, 106588-06-1; $(\text{RuCl}_2(\text{COD}))_n$, 50982-13-3.

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Nature of the Lowest Energy Excited State in Vanadium(II) Polypyridine Complexes

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There is extensive literature on the photochemical and photophysical properties of $\text{Cr}(\text{NN})_3^{3+}$ ($\text{NN} = \text{polypyridine ligand}$).¹ Our recent studies of the isoelectronic vanadium(II) complexes have demonstrated the initial photooxidation of $\text{V}(\text{NN})_3^{2+}$ to $\text{V}_2(\text{NN})_4(\mu\text{-OH})_2^{4+}$.² This ion can be oxidized further to vanadium(IV), and the two redox steps can be combined in a photoinitiated two-electron process.³ However, the efficiency of these photoredox reactions is limited by the extremely short excited-state lifetimes of $\text{V}(\text{NN})_3^{2+}$ (less than 2 ns in solution at room temperature²). The photophysical experiments described herein establish that the lowest excited states in these complexes are primarily quartet MLCT (metal to ligand charge transfer) in character.

Experimental Section

The ligands 4,7-diphenyl-1,10-phenanthroline, 4,4'-dimethyl-2,2'-bipyridine, and 3,4,7,8-tetramethyl-1,10-phenanthroline (Ph_2phen , Me_2bpy , and Me_4phen , respectively) and other chemicals and solvents were reagent or spectrophotometric grade and were used as received. The method of ref 2 was used to prepare the new vanadium(II) complexes. Anal. Calcd for $\text{C}_{74}\text{H}_{48}\text{F}_6\text{N}_6\text{O}_6\text{S}_2\text{V}$ ($[\text{V}(\text{Ph}_2\text{phen})_3](\text{O}_3\text{SCF}_3)_2$): C, 66.02; H, 3.59; F, 8.47; N, 6.24. Found: C, 66.10; H, 3.59; F, 8.34; N, 6.18. Calcd for $\text{C}_{50}\text{H}_{48}\text{F}_6\text{N}_6\text{O}_6\text{S}_2\text{V}$ ($[\text{V}(\text{Me}_4\text{phen})_3](\text{O}_3\text{SCF}_3)_2$): C, 56.76; H, 4.57; F, 10.77; N, 7.94. Found: C, 55.41; H, 4.57; F, 10.16;

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