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Synthesis of an Ionic Paramagnetic Ruthenium(III) Complex and Its Application as an Efficient and Recyclable Catalyst for the Transfer Hydrogenation of Ketones

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A novel ionic complex, bis[1-butyl-2-(diphenylphosphanyl)-3-methylimidazolium]tetrachloridoruthenium(III) hexafluorophosphate (**2**), has been synthesized and fully characterized. The single-crystal X-ray diffraction analysis showed that **2** is composed of an Ru complex cation and PF_6^- anion. The cation has a highly symmetrical Ru-centered octahedron geometry with four Cl atoms in the equatorial plane and two imidazolium-substituted phosphane ligands in the axial positions. It exhibits paramagnetism due to the presence of one unpaired electron in the phosphane-ligated low-spin Ru^{III} complex. Complex **2** exhibited good catalytic performance in the transfer hydrogenation of a wide range of ketones by using alcohols as hydrogen donors. Owing to its high polarity, good thermal stability, and insensitivity to moisture and oxygen, complex **2** could be used in six catalytic cycles in the transfer hydrogenation of acetophenone without any obvious loss of activity.

Introduction

The reduction of carbonyl compounds to alcohols is an industrially important reaction for the preparation of fine chemicals, perfumes, agrochemicals, and pharmaceuticals.[1] Methods for the metal-catalyzed transformation of carbonyl compounds into alcohols include hydrogenation by H_2, transfer hydrogenation, and hydrosilylation.[2–4] Transfer hydrogenation is a particularly useful protocol in which unsaturated compounds can be hydrogenated without the use of molecular H_2. In comparison with hydrogenation by H_2 or with a hydride reagent, transfer hydrogenation is attractive due to its operational simplicity and the reduction of risk associated with the use of high pressure, which are beneficial for large-scale production from environmental and economic points of view.[5] Transition-metal complexes have been extensively investigated as catalysts for the transfer hydrogenation of ketones to secondary alcohols.[6–8] Ruthenium(II) complexes bearing N-heterocyclic carbenes (NHCs), phosphanes, diamines, aminodiphosphanes, amine–bis(phenolate)s, chiral ligands, and heterocyclic ligands[5–16] are the most prominent catalysts and exhibit high activities in the transfer hydrogenation of ketones. In contrast to electron-rich ligands as strong σ-donors,[17] electron-deficient ligands are less explored.[18] Few catalytic processes have been shown to benefit from the use of electron-deficient ligands,[19] particularly when the Lewis acidity of the metal center is crucial.[20] Cationic phosphanes bearing quaternary ammonium moieties possessing electron-deficient character,[21] such as the amidiniophosphane ligands with a positive charge vicinal to the P^{III} atom,[22] are, however, of great interest in organometallic chemistry and catalysis.[23]

Compared with Ru^{II} analogues, there exist relatively few reported examples of paramagnetic Ru^{III} complexes containing tertiary phosphanes[24] and their application to transfer hydrogenation. On the other hand, the recycling of homogeneous ruthenium complex catalysts is still a challenging problem due to difficult separation workup and rapid deactivation.

In this work, a novel ionic paramagnetic ruthenium(III) complex, bis[1-butyl-2-(diphenylphosphanyl)-3-methylimidazolium]tetrachloridoruthenium(III) hexafluorophosphate (**2**), was synthesized by the complexation of the ionic imidazolium-substituted phosphane ligand **1** and hydrated ruthenium(III) chloride. Detailed crystallographic data for **2** are reported. The catalytic performance and recyclability of **2** for the reduction of ketones to the corresponding alcohols by transfer hydrogenation have been fully investigated (Scheme 1).

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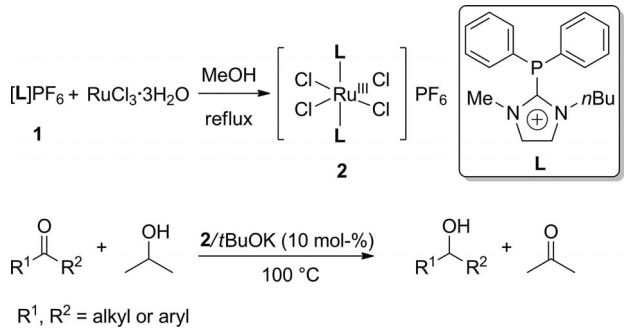

Scheme 1. Synthesis of **2** as a catalyst precursor for the transfer hydrogenation of ketones.

Results and Discussion

Synthesis and Characterization of 2

Complex **2** was prepared by applying procedures similar to those used for the preparation of $[Ru^{II}Cl_2(PPh_3)_3]$.[25] It was assumed that a structurally similar complex would be obtained by replacing the PPh_3 ligand with **1**[26] and allowing **1** to coordinate to $RuCl_3{\cdot}3H_2O$. However, surprisingly, a novel complex in which the Ru ion is in a valence state of +3 was obtained. Complex **2**, which was isolated as an orange solid in good yield (75 wt.-%), is air- and moisture-stable both in the solid state and in organic solvents at room temperature. But dmso could not be used as a solvent for **2** due to the displacement of the ligand **L** by dmso. Single crystals for X-ray diffraction analysis were obtained by recrystallization from acetone/hexane.

The molecular structure of **2** is depicted in Figure 1. It is composed of the Ru complex cation and PF_6^- anion. The Ru complex cation exhibits an ideal octahedral geometry with the Ru^{III} (d^5) ion situated exactly in the center of the octahedron and hexacoordinated by four chlorine atoms in the equatorial plane and two imidazolium-substituted phosphane ligands in the axial positions. The bond angles of P1–Ru1–P1a, Cl1–Ru1–Cl1a, and Cl2–Ru1–Cl2a are 180° (Table 1). The two Ru–P bond lengths are the same at 2.408(1) Å, much longer than the classical values (2.2–2.3 Å) in typical phosphane-ligated Ru^{II} complexes.[25,27,28] As **L** is an electron-deficient ligand relative to PPh_3, the length of the Ru–P bond can be attributed to an enhanced partial ionic character of the Ru–P bond of the type $[\mathbf{L}RuCl_4]\mathbf{L}^+$. This particular feature could be dictated by the +3 oxidation state of the Ru center: Indeed, imidazoliophosphanes bearing a positively charged imidazolium moiety similar to **L** have been reported to afford typical covalent complexes with much less electronegative metal centers (M = Pd^{II}, Rh^{I}) in which the M–P bond lengths are in the classical range.[22,29,30]

The Ru center in **2** may have a +3 valance state for HSAB (hard-soft acid-base theory) reasons. The cationic phosphane of **L** is harder than that of PPh_3, which is compatible with a hard Ru^{III} center. It is also believed that the reduction of Ru^{III} to Ru^{II} in the formation of $[Rh^{II}Cl_2(PPh_3)_3]$ could be accomplished by PPh_3 as a strong electron donor and a good reducing reagent. In contrast, **L** is a relatively weak electron donor with weakened reduction ability. Consequently, the redox reaction between **1** and $RuCl_3{\cdot}3H_2O$ during the complexation was avoided, leading to an unchanged valance state for Ru^{3+}.

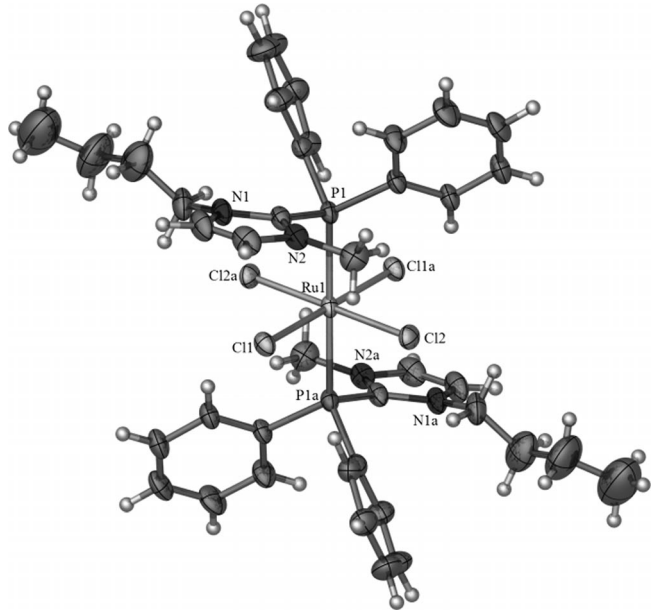

Figure 1. Molecular structure of **2** (anion PF_6^- and the solvent molecule, acetone, have been omitted for clarity).

Table 1. Selected bond lengths [Å] and bond angles [°] for **2**.

Ru1–Cl1	2.363(1)	Ru1–Cl1a	2.363(1)
Ru1–Cl2	2.344(1)	Ru1–Cl2a	2.344(1)
Ru1–P1	2.408(1)	Ru1–P1a	2.408(1)
Cl2–Ru1–Cl1	89.63(4)	Cl2a–Ru1–Cl1	90.37(4)
Cl2–Ru1–Cl1a	90.37(4)	Cl2a–Ru1–Cl1a	89.63(4)
Cl2–Ru1–P1	90.59(4)	Cl2a–Ru1–P1	89.41(4)
Cl1–Ru1–P1	90.28(4)	Cl1a–Ru1–P1	89.72(4)
Cl2–Ru1–P1a	89.41(4)	Cl2a–Ru1–P1a	90.59(4)
Cl1–Ru1–P1a	89.72(4)	Cl1a–Ru1–P1a	90.28(4)
Cl2–Ru1–Cl2a	180.00(5)	Cl1–Ru1–Cl1a	180.0
P1–Ru1–P1a	180.0		

The cation $[RuCl_4L_2]^+$ in **2** is formally a 17-electron complex, which is supposed to be unstable, whereas in the resonance structure of $[\mathbf{L}RuCl_4]\mathbf{L}^+$, the Ru^{III} center is formally a 15-electron complex. The contribution to both forms in the resonating description corresponds to a stabilized average of a 16-electron cationic complex. On the other hand, the highly symmetrical octahedral configuration further facilitates the stability of $[RuCl_4L_2]^+$ in **2**. In addition, **1** is characterized by strong oxidation tolerance due to its electron-deficient nature; the corresponding complex of **2** with partial ionic character is also moisture- and air-insensitive at room temperature. TG/DTA analysis indicated that **2** thermally decomposed in air at 205 °C, revealing its good thermal stability.

Because **2** is in a low-spin state with an indication of the presence of one unpaired electron in the Ru^{III} center,[12] it has a paramagnetic nature. Consequently, the ^1H and ^{31}P

NMR signals attributed to **L** in the cationic complex are broadened to flatness. However, the ^{31}P NMR spectrum still shows the signal of the PF_6^- counteranion at δ = –143.1 ppm, consistent with its solid-state structure, due to the negligible influence of Ru^{III} magnetic moments on the counteranion.

Catalytic Performance of 2 in Transfer Hydrogenation

Transfer hydrogenation catalyzed by **2** was investigated by using acetophenone as a model substrate with 2-propanol as the hydrogen donor under solvent-free conditions (Table 2). 2-Propanol is inexpensive and easy to handle (b.p. 82 °C) and the volatile acetone that is formed can also be easily removed in the separation process. Because the catalytic performance of the ruthenium complexes could be improved dramatically under alkaline conditions,[3] *t*BuOK was chosen as the optimal promoter after screening the bases K_2CO_3, KOH, and *t*BuOK. In the absence of base, transfer hydrogenation of acetophenone did not occur. For comparison, $[Ru^{II}Cl_2(PPh_3)_3]$ and $RuCl_3{\cdot}3H_2O$ were also used as catalysts. As shown in Table 2, used fresh, **2** and $[Ru^{II}Cl_2(PPh_3)_3]$ exhibit competitive activities irrespective of whether the Ru ion is in a valence state of +3 or +2 (Entries 2 and 4). However, transfer hydrogenation did not occur with $RuCl_3{\cdot}3H_2O$, that is, in the absence of phosphane ligation (Entry 3).

Table 2. Transfer hydrogenation of acetophenone catalyzed by different Ru catalysts.[a]

Entry	Catalyst	Time [h]	Conv. [%][b]	Sel. [%][b]	TOF [h^{-1}][c]
1	**2**	1	47	100	31
2	**2**	2	87	100	29
3	$RuCl_3{\cdot}3H_2O$	2	–	–	–
4	$[Ru^{II}Cl_2(PPh_3)_3]$	2	86	100	29

[a] Catalyst (1.5 mol-%), acetophenone (5 mmol), 2-propanol (3 mL), , *t*BuOK (10 mol-%), reaction temperature 100 °C. [b] Determined by GC. [c] TOF = turnover frequency.

The recovery and recycling of homogeneous Ru catalysts in transfer hydrogenation are important from an economic point of view due to the high cost of ruthenium compounds as well as for preventing the contamination of the final products by toxic metals. Thus, recycling experiments were conducted by using complex **2** in the transfer hydrogenation of acetophenone. The results in Table 3 show that **2** could be used five times without any obvious activity loss. However, in the sixth run, the conversion of acetophenone decreased to 77%, mainly due to the manipulative loss of the catalyst. In each run, upon completion, the organic compounds, including acetophenone, 1-phenylethanol, 2-propanol, and acetone, were extracted with petroleum ether for GC analysis. The leaching of Ru into the extracted organic phase was below the detection limit of ICP (<0.1 μg/g) due to the high polarity of **2** as a result of the imidazolium ring, which has been recognized as a useful technique for preventing metal catalysts from leaching.[31] Because **2** is thermally stable (thermal decomposition temperature 205 °C) and insensitive to moisture and oxygen, **2** could be recovered in water and open air, which facilitated the separation workup greatly. In contrast, the recovery and recycling of the $[Ru^{II}Cl_2(PPh_3)_3]$ catalyst were unsuccessful.

Table 3. Recycling of **2** as catalyst in the transfer hydrogenation of acetophenone.[a]

Run[b]	Conv. [%][c]	Sel. [%][c]	TOF [h^{-1}]
1	87	100	29
2	84	100	28
3	85	100	28
4	81	100	27
5	86	100	29
6	77	100	26

[a] Complex **2** (1.5 mol-%), acetophenone (5 mmol), 2-propanol (3 mL), *t*BuOK (10 mol-%), reaction temperature 100 °C, reaction time 2 h. [b] *t*BuOK (10 mol-%) was added to each run. [c] Determined by GC.

In fact, **2** is only a catalyst precursor. During the catalytic reaction, derivation of **2** to the catalytic species must occur. This derivation of **2** was monitored during the recycling by ^{31}P NMR spectroscopy (Figure 2). Upon completion of each run, the reaction mixture was extracted with the ionic liquid (IL) of $[Bpy]BF_4$ (*N*-*n*-butylpyridinium tetrafluoroborate, 2 mL) for ^{31}P NMR analysis. Because $[Bmim]BF_4$ (1-*n*-butyl-3-methylimidazolium tetrafluoroborate) can act as a potential NHC ligand, $[Bpy]BF_4$ with noncoordinating ability was selected as the extracting reagent for the polar Ru-based catalyst to rule out any possible coordination influence. The IL extract obtained was analyzed by ^{31}P NMR spectroscopy directly at ambient temperature. An unidentified signal (δ = 16 ppm; Figure 2) that did not belong to **2** (no signal) or **L** (δ = –28.5 ppm) was observed throughout the recycling experiments. It was proven that the species with the chemical shift at δ = 16 ppm was responsible for

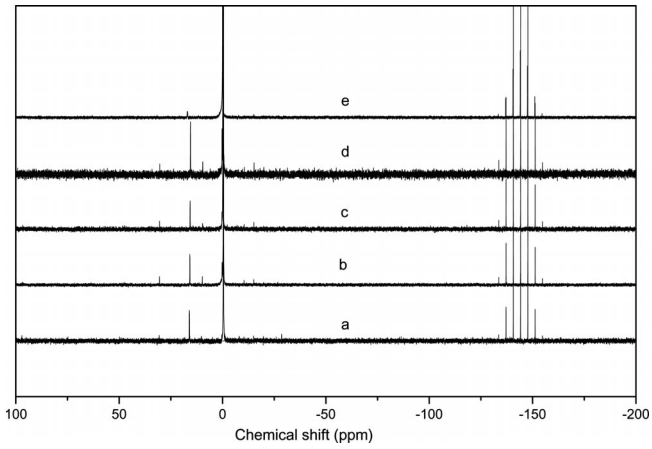

Figure 2. Evolution of **2** in the recycling experiments reported in Table 3 recorded by proton-decoupled ^{31}P NMR spectroscopy (a: IL extract after 1st run; b: IL extract after 2nd run; c: IL extract after 3rd run; d: IL extract after 4th run; e: IL extract after 5th run).

Table 4. Transfer hydrogenation of different ketones catalyzed by **2**.[a]

Entry	Ketone	Alcohol	Conv. [%][b]	Sel. [%][b]	TOF [h^{-1}]
1	acetophenone	2-propanol	87	100	29
2	benzophenone	2-propanol	91	100	31
3	cyclohexanone	2-propanol	99	100	33
4	2-adamantanone	2-propanol	98	100	33
5	1-methylpyrrolidin-2-one	2-propanol	–	–	–
6	chalcone	2-propanol	99	93[c]	31
7	3,5,5-trimethylcyclohex-2-enone	2-propanol	49	74[d]	12
8	6-methylhept-5-en-2-one	2-propanol	90	85[e]	26
9	octan-2-one	2-propanol	91	100	31
10	heptan-4-one	2-propanol	70	100	23
11[f]	acetophenone	2-hexanol	70	100	16
12[g]	cyclohexanone	2-phenylethanol	80	100	11

[a] Complex **2** (1.5 mol-%), ketone (5 mmol), alcohol (3 mL), *t*BuOK (10 mol-%), temperature 100 °C, time 2 h. [b] Determined by GC and GC–MS. [c] Major product was 1,3-diphenylpropan-1-one. The byproduct was 3,5-diphenylcyclohex-2-enone. [d] Major product was 3,3,5-trimethylcyclohexanone. The byproduct was 3,3,5-trimethylcyclohexanol. [e] Major product was 6-methylheptan-2-one. The byproduct was 6-methylheptan-2-ol. [f] Time 3 h. [g] Time 5 h.

the catalytic transformation of acetophenone into 1-phenylethanol. Without the formation of this species in the absence of *t*BuOK in the reaction, the reduction of acetophenone by 2-propanol did not occur. Thus, the species with the signal observed at δ = 16 ppm can be attributed to the Ru^{II}–P-based catalytic species derived from **2**, but not to a free phosphane derivative such as $HP(O)Ph_2$. The latter could be formed upon cleavage of the N_2C^+–P bond in **2**. The good stability of the real catalytic Ru^{II}–P species in the transfer hydrogenation, which is not silent in ^{31}P NMR spectroscopy due to its diamagnetism, could account for the recyclability of **2**. However, at this stage, without any further analytic evidence, it is difficult to determine whether the signal at δ = 16 ppm in Figure 2 can be ascribed to the formation of an NHC–Ru complex with the P ligand or others.

To examine the generality of **2** as a catalyst for transfer hydrogenation, the scope of ketones with different electronic and steric effects was investigated under similar conditions (Table 4). Benzophenone with a large steric hindrance was converted into diphenylmethanol even faster than acetophenone, implying facial access of the substrate to catalyst **2** (Entry 2 vs. 1). With cyclohexanone and 2-adamantanone, efficient transfer hydrogenations were achieved with excellent conversion and 100% selectivity to the corresponding alcohols, because the C=O group is directed out of the six-membered ring (Entries 3 and 4). However, the hydrogenation of 1-methylpyrrolidin-2-one was not observed, probably due to its potential coordination to the Ru center as an N-containing ligand (Entry 5). With the unsaturated ketones, chalcone was converted into 1,3-diphenylpropan-1-one in high yield due to the reduction of only the C=C bond. The Michael addition of chalcone with 2-propanol and subsequent aldol condensation led to the formation of 3,5-diphenylcyclohex-2-enone as a byproduct. The reduction of the C=O bond in chalcone was not observed (Entry 6). For both 3,5,5-trimethylcyclohex-2-enone and 6-methylhept-5-en-2-one, the major products were obtained by the reduction of only the C=C bond, whereas the minor products obtained were a result of the reduction of both the C=C and C=O bonds (Entries 7 and 8), revealing the poor chemoselective reduction of the C=O bond with **2** as catalyst for unsaturated ketone substrates. The aliphatic ketones octan-2-one and heptan-4-one were converted into the secondary alcohols in good conversions and with excellent selectivities (Entries 9 and 10). It was also found that when 2-hexanol and 2-phenylethanol were used as the hydrogen donors in place of 2-propanol, the transfer hydrogenation occurred efficiently (Entries 11 and 12). However, the reduction of aldehydes to primary alcohols with controlled chemoselectivity by transfer hydrogenation is considered rather difficult due to the side-reaction that occurs under basic conditions.

Conclusions

The paramagnetic ionic ruthenium complex of **2**, in which the Ru ion is in the valence state of +3, has been synthesized for the first time. The single-crystal X-ray structure of **2** shows a highly symmetrical Ru^{III}-centered octahedron cation with PF_6^- as the counteranion. As a result of its high polarity, good thermal stability, and insensitivity to moisture and oxygen, complex **2** proved to be an efficient and recyclable precatalyst for the transfer hydrogenation of a wide range of ketones when using alcohols as hydrogen donors.

Experimental Section

Reagents and Analysis: All syntheses were carried out under nitrogen by using standard Schlenk techniques. All reagents were purchased from Aladin Reagent Co., Shanghai, China and used as received. The FTIR spectra were recorded with a Nicolet NEXUS 670 spectrometer. The ^1H and ^{31}P NMR spectra were recorded with a Bruker Avance 500 spectrometer. The ^{31}P NMR spectra were referenced to 85% H_3PO_4 sealed in a capillary tube as an internal standard. Elemental analyses for CHN were obtained by using an Elementar Vario EL III instrument, whereas the amount of Ru in the sample was quantified by using an inductive coupled plasma atomic emission spectrometer (ICP-AES) equipped with an IRIS

Intrepid II XSP instrument (Thermo Electron Corporation). TG/DTA was performed with a Mettler TGA/SDTA 851^e instrument and STARe thermal analysis data processing system. TG/DTA analysis was performed in a flow of air with a temperature ramp of 10 °C min^{-1} between 50 and 800 °C. GC analysis was performed with a Shimadzu-2014 instrument equipped with a Rtx-Wax capillary column (30 m × 0.25 mm × 0.25 μm). GC–MS was performed with an Agilent 6890 instrument equipped with an Agilent 5973 mass-selective detector.

Synthesis

1-Butyl-2-(diphenylphosphanyl)-3-methylimidazolium Hexafluorophosphate (1): Salt **1** was prepared according to published methods[19] but with some modifications. Under nitrogen, a solution of 1-butyl-3-methylimidazolium hexafluorophosphate (15.0 g, 53.0 mmol) in dry CH_2Cl_2 (50 mL; previously heated at reflux with calcium hydride and freshly distilled) was cooled to –78 °C, and *n*BuLi (27 mL, 2.2 M in hexane, 59.4 mmol) was added dropwise. After stirring the solution for 1 h, chlorodiphenylphosphane (PPh_2Cl; 11.7 g, 53.0 mmol) was added dropwise. The resultant mixture was stirred overnight and the reaction temperature was increased to ambient. After quenching excess *n*BuLi with deionized water, the solvent was removed in vacuo. The residue was recrystallized from EtOH to yield **1** as a white solid (yield: 18.5 g, 75 wt.-%). ^{1}H NMR ($CDCl_3$): δ = 0.78 (t, J = 8.0 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.15 (m, 2 H, $CH_2CH_2CH_2CH_3$), 1.56 (m, 2 H, $CH_2CH_2CH_2CH_3$), 3.48 (s, 3 H, NCH_3), 4.26 (t, J = 7.8 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 7.30 [m, 4 H, $CH_3NCP(Ph_2)N^+$], 7.49 [m, 6 H, $CH_3NCP(Ph_2)N^+$], 7.59 [s, 1 H, $NC(H)C(H)N^+$], 7.62 [s, 1 H, $NC(H)C(H)N^+$] ppm. ^{31}P NMR ($CDCl_3$): δ = –28.5 (s, PPh_2), –143.5 (sept, PF_6) ppm.

Bis[1-butyl-2-(diphenylphosphanyl)-3-methylimidazolium]tetrachloridoruthenium(III) Hexafluorophosphate (2): Under N_2, a solution of $RuCl_3 \cdot 3H_2O$ (0.5 g, 1.8 mmol) in methanol (20 mL) was heated at reflux for 10 min and then cooled to room temperature. Salt **1** (3.4 g, 7.2 mmol) was then added. The resulting mixture was stirred under reflux for 8 h. The solid obtained was washed with alcohol and diethyl ether, and dried in vacuo to give **2** as an orange powder (yield: 1.5 g, 75 wt.-%), which was recrystallized from acetone/hexane. TG/DTA (in air flow): The thermal decomposition temperature of **2** was 205 °C. FTIR (KBr pellet): $\tilde{\nu}$ = 3737 (w), 3447 (w), 2960 (s), 1620 (w), 1395 (m), 1260 (m), 841 (P–F, s) cm^{-1}. As a result of the paramagnetic nature of the Ru^{III} complex, the ^{1}H and ^{31}P NMR signals of **2** (in [D_6]acetone) attributed to the phosphane ligand were broadened to flatness, but the ^{31}P NMR ([D_6]acetone) signal attributed to the PF_6^- counteranion was observed clearly at δ = –143.5 ppm (sept). $C_{40}H_{48}Cl_4F_6N_4P_3Ru$ (1035): calcd. C 46.4, H 4.68, N 5.42; found C 45.6, H 4.58, N 5.20.

X-ray Crystallography: Intensity data for **2** were collected at room temperature (296 K) with a Bruker SMARTAPEX II diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data reduction included absorption corrections by the multiscan method. The structure was solved by direct methods and refined by full-matrix least squares using SHELXS-97[32] with all non-hydrogen atoms refined anisotropically. Hydrogen atoms were included in their geometrically ideal positions and refined isotropically. Crystal data and refinement details are given in Table 5. CCDC-805636 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 5. Crystal data and structure refinement for **2**.

	2·2$(CH_3)_2(CO)$
Empirical formula	$C_{46}H_{60}Cl_4F_6N_4O_2P_3Ru$
Formula mass	1150.76
Crystal system	monoclinic
Space group	*C*2/*c*
a [Å]	25.2640(9)
b [Å]	9.7111(3)
c [Å]	22.9382(8)
α [°]	90
β [°]	104.148
γ [°]	90
V [Å^3]	5457.0(3)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.401
μ(Mo-K_α) [mm^{-1}]	0.630
T [K]	296(2)
λ	0.71073
Total reflections	30584
Unique reflections (R_{int})	4777 (0.0219)
R_1 [$I > 2\sigma(I)$]	0.0449
wR_2 (all data)	0.1354
F(000)	2364

General Procedure for the Transfer Hydrogenation Catalyzed by 2: In a typical experiment, the isolated crystalline **2** (0.075 mmol) was mixed sequentially with acetophenone (5 mmol), 2-propanol (3 mL, excess), and a base. The homogeneous mixture obtained was purged with N_2 and then stirred vigorously in a sealed Teflon-lined stainless-steel autoclave. Upon completion, distilled water (5 mL) was added, and the mixture was stirred vigorously. Then the solution was extracted with petroleum ether (5 mL × 3). The combined petroleum ether extracts were analyzed by GC to determine the conversions (*n*-dodecane as internal standard) and selectivities (normalization method). The products were further identified by GC–MS. The remaining aqueous solution was dried under vacuum to afford the residue for further use.

Acknowledgments

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