Half-Sandwich Chloro Complexes as Ligands for $RuCl_2L_2$ (L = PR_3, alkene): Syntheses, Structures, and Catalytic Activity of New Homo- and Heterobimetallic Complexes

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Homo- and heterobimetallic complexes, in which half-sandwich complexes of ruthenium(II), rhodium(III), and iridium(III) are connected via three chloro bridges to $RuCl_2(PPh_3)_2$, have been synthesized. The complexes were obtained in quantitative yields by reaction of [(cymene)RuCl(μ-Cl)]$_2$ or [Cp*MCl(μ-Cl)]$_2$ (M = Rh, Ir) with [$(PPh_3)_2$ClRu(μ-Cl)$_3$Ru(Me_2CO)$(PPh_3)_2$] (**2**). The crystal structure of **2** has been determined by X-ray analysis. Evidence that half-sandwich chloro complexes are generally suited for stabilizing $RuCl_2L_2$ fragments is provided by the synthesis of complexes [(cymene)Ru(μ-Cl)$_3$RuCl(dppb)] [dppb = 1,4-bis(diphenylphosphanyl)butane] and [(cymene)Ru(μ-Cl)$_3$RuCl(cod)] (cod = 1,5-cyclooctadiene), both of which have been structurally characterized. The abilities of all the complexes to catalyze the oxidation of secondary alcohols with 2-butanone have been investigated. The complex [Cp*Rh(μ-Cl)$_3$RuCl$(PPh_3)_2$] has proved to be highly active, displaying a performance superior to that of previously known catalysts such as [$RuCl_2(PPh_3)_3$]. Using a substrate/catalyst ratio of 500:1, initial turnover frequencies of up to 3400 h^{-1} were observed. The potential of these types of bimetallic complexes to act as catalysts for other reactions is discussed.

Introduction

Inspired by Nature, specifically by the high efficiencies and selectivities of bimetallic metalloenzymes, chemists have tried hard to design polynuclear complexes showing superior performances in catalytic reactions. Despite numerous efforts, often accompanied with elaborate syntheses of suitable ligands, success has hitherto been rare, especially in relation to catalysts with relevance in organic synthesis.[1] Prominent exceptions are the heterometallic lanthanide complexes developed by Shibasaki et al., which are excellent catalysts for asymmetric aldol and nitro-Mannich-type reactions,[2] and a dinuclear rhodium complex that has been used in hydroformylation reactions.[3]

We have investigated the syntheses, structures, and reactivities of dinuclear complexes in which two different metal fragments are connected by halo bridges.[4] A major advantage of this kind of compound is that the synthesis is generally fast and easy. Consequently, a variety of different complexes can be obtained in a short time, allowing an efficient screening of their catalytic properties.

The first convincing evidence that highly active catalysts can be found within this class of compounds was recently provided by the groups of Grubbs and Herrmann. Studying metathesis reactions with well-defined (carbene)ruthenium complexes, they discovered that dinuclear complexes in which ruthenium, osmium, and rhodium complexes are connected by chloro bridges to a ruthenium fragment are exceptionally active.[5] Importantly, the catalytic activity of the carbene complex is modulated by the second metal fragment, which itself does not participate directly in the catalytic reaction.

We describe herein the synthesis and structures of new homo- and heterobimetallic complexes containing $RuCl_2L_2$ fragments (L = PR_3, alkene). The formally unsaturated 14-electron species are coordinated to half-sandwich complexes of ruthenium, rhodium, and iridium via three chloro bridges. The catalytic oxidation of secondary alcohols by 2-butanone with these types of bimetallic complexes is reported.

Results and Discussion

Synthesis of Dinuclear Complexes with $RuCl_2(PR_3)_2$ Fragments

[$RuCl_2(PPh_3)_3$] is a remarkably versatile catalyst precursor. Catalytic reactions such as hydrogenations, isomerizations, oxidations, and hydrosilylations have been carried out with this complex, in some cases with remarkable efficiency.[6] A major drawback of [$RuCl_2(PPh_3)_3$], however, is its low solubility in organic solvents. For several reactions, the loss of one triphenylphosphane ligand is assumed to occur prior to catalysis. We were thus interested in ascertaining whether organometallic chloro complexes of the late transition metals could be used to stabilize and solubilize the active $RuCl_2(PPh_3)_2$ fragment. In a first experiment, we investigated the reaction of [(cymene)RuCl(μ-Cl)]$_2$ with [$RuCl_2(PPh_3)_3$] in dichloromethane (Scheme 1).

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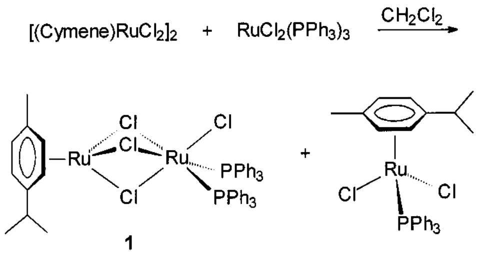


Scheme 1. Synthesis of complex **1**

Equimolar amounts of two products were formed, one of which was identified as [(cymene)$RuCl_2(PPh_3)$] by NMR (^1H, ^{31}P). The second product (**1**) was isolated in pure form by washing the mixture with acetone. Spectroscopic as well as analytical data pointed to a complex of the empirical formula [Ru_2Cl_4(cymene)$(PPh_3)_2$]. The geometry of **1** was established by a single-crystal X-ray analysis, which revealed a structure with three bridging chloro ligands. This geometry is what was expected in view of the high tendency of (arene)-[7] as well as (phosphane)ruthenium(II) complexes[6c] to form (μ-Cl)$_3$ structures. Unfortunately, despite numerous attempts, we were unable to obtain crystallographic data of satisfactory quality and therefore a more detailed analysis of the structure of **1** is not presented.

In a quest for a more suitable source of the $RuCl_2(PPh_3)_2$ fragment, we turned our attention to a complex of the stoichiometry $[RuCl_2(PPh_3)_2(Me_2CO)]_n$ (**2**). Wilkinson first synthesized this compound by heating $[RuCl_2(PPh_3)_3]$ in acetone under reflux.[8] Later, a dimeric structure with two bridging chloro ligands was suggested,[9] but problems in reproducing the reaction were also reported.[10] We have found that a complex of this formula can be obtained if $[RuCl_2(PPh_3)_3]$ is treated with acetone at room temperature. The heterogeneous reaction is best carried out without stirring. Under these conditions, dark-red crystals of **2** are formed in good yield after several days. The crystals, which can be stored without the need for an inert gas, display very low solubility in all common organic solvents. The molecular structure of **2** in the crystal is shown in Figure 1. The complex is dimeric but, contrary to previous suggestions, three and not two chloro bridges are observed. Consequently, the second molecule of acetone is not coordinated to the ruthenium center. Therefore, complex **2** should be formulated as $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(Me_2CO)(PPh_3)_2]Me_2CO$.

The geometry about the ruthenium atoms can be described as distorted octahedral. The distortion is mainly due to the sterically demanding phosphane ligands and is manifested in large P−Ru−P angles (98.2 and 99.7°). In agreement with general theoretical investigations,[11] the acetone ligand shows an η^1 and not an η^2 coordination mode. The C−O bond length in the coordinated acetone molecule is slightly longer (1.20 Å) than the C−O bond length in the co-crystallized "free" acetone molecule (1.17 Å). The structural motif found for **2** is common in (phosphane)ruthenium chemistry. Several other complexes of the general formula $[(PR_3)_2ClRu(\mu\text{-}Cl)_3Ru(L)(PR_3)_2]$ (L = neutral or anionic ligand) have been described.[6c,12] Structural data for the closely related $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(CS)(PPh_3)_2]$ are available.[13]

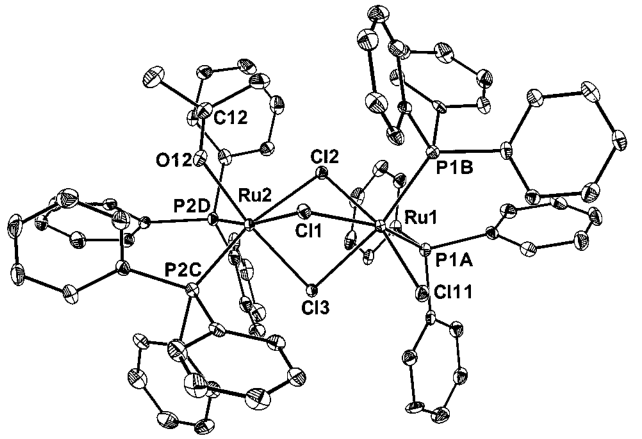
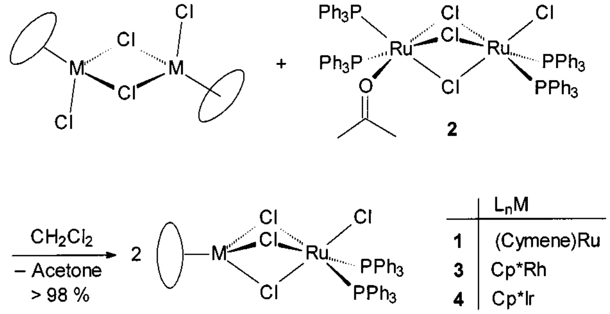


Figure 1. Molecular structure of **2** in the crystal; the solvent molecule and hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Ru1−Cl1 2.540(2), Ru1−Cl2 2.395(2), Ru1−Cl3 2.450(2), Ru2−Cl1 2.446(2), Ru2−Cl2 2.470(2), Ru2−Cl3 2.368(2), Ru1−Cl11 2.400(2), Ru1−P1A 2.268(2), Ru1−P1B 2.293(2), Ru2−P2C 2.300(2), Ru2−P2D 2.316(2), Ru2−O12 2.121(4), O12−C12 1.201(8); Ru1−Cl3−Ru2 83.19(5), P1A−Ru1−P1B 98.23(6), Cl2−Ru1−Cl11 165.04(5), P2C−Ru2−P2D 99.71(6)

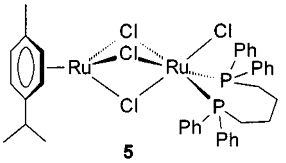
Complex **2** proved to be an ideal starting material for the synthesis of **1** and the heterobimetallic complexes **3** and **4**. Upon reaction of **2** with [(cymene)RuCl(μ-Cl)]$_2$ or [Cp*MCl(μ-Cl)]$_2$ (M = Rh, Ir) in dichloromethane, the dinuclear compounds were obtained in quantitative yields (Scheme 2).



Scheme 2. Synthesis of the homo- and heterobimetallic complexes **1**, **3**, and **4**

Compounds **3** and **4** are among the first heterobimetallic complexes with three chloro bridges to be synthesized.[14] Heterobimetallic $Rh^{III}-Ru^{II}$ complexes with bridging hydrido and carboxylato ligands have been described by Süss-Fink.[15] In contrast to $[RuCl_2(PPh_3)_3]$, the new complexes show good solubility in a variety of organic solvents, such as dichloromethane, tetrahydrofuran, and benzene, a prerequisite for applications in homogeneous catalysis. Although they are not very sensitive towards oxygen in the solid state, solutions of **1**, **3**, and **4** readily turn brown upon exposure to air.

For catalytic applications, ruthenium complexes with chelating phosphane ligands are especially interesting since the accessibility of the active site can be controlled by the bite angle of the chelate. Furthermore, stereochemical information can be introduced using chiral ligands. To demonstrate that half-sandwich chloro complexes are suited for stabilizing $RuCl_2(L-L)$ complexes [L−L = bis(phosphane)], we have synthesized complex **5** by reaction of $[RuCl_2(PPh_3)(dppb)]$ with $[(cymene)RuCl(\mu\text{-}Cl)]_2$; $[(cymene)RuCl_2(PPh_3)]$, which is formed as a side product, can be separated by crystallization from acetone.



5

The structure of complex **5** in the crystal is shown in Figure 2. As expected, the (η^6-arene)Ru fragment is coordinated via three chloro bridges to the second ruthenium atom, the geometry about which can be described as distorted octahedral. The Ru−Cl bond length to the terminal chloro ligand (2.39 Å) is smaller than the Ru−Cl distances of the bridging chloro ligands (2.41−2.53 Å). The P−Ru−P bond angle (94.2°) is comparable to those found in other Ru(dppb) complexes.[16]

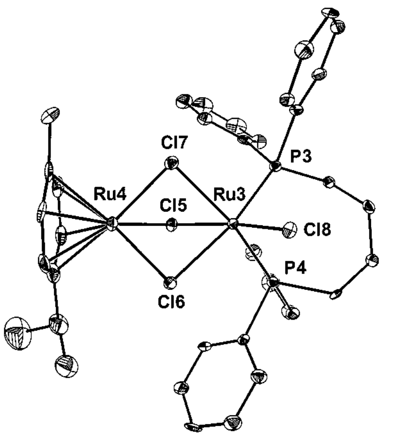
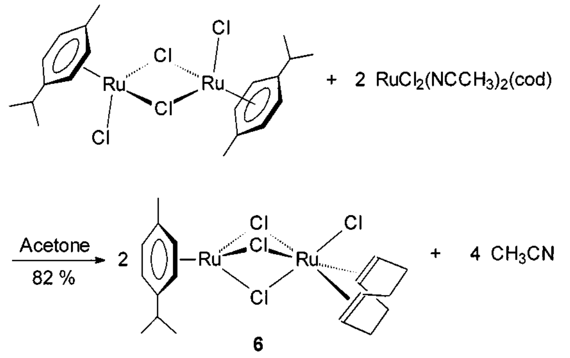


Figure 2. Molecular structure of **5** in the crystal; hydrogen atoms and solvent molecules are omitted for clarity; selected bond lengths [Å] and angles [°]: Ru4−Cl5 2.425(2), Ru4−Cl6 2.410(2), Ru3−Cl6 2.535(2), Ru4−Cl7 2.438(2), Ru3−Cl5 2.407(2), Ru3−Cl7 2.534(2), Ru3−P3 2.240(2), Ru3−P4 2.249(2), Ru3−Cl8 2.387(2); Ru3−Cl5−Ru4 86.17(6), P3−Ru3−P4 94.24(7), Cl8−Ru3−Cl5 166.99(7), P4−Ru3−Cl5 94.63(6)

Synthesis of a Dinuclear Complex with an $RuCl_2$(cod) Fragment

To investigate whether half-sandwich chloro complexes can form dinuclear complexes with other $RuCl_2L_2$ fragments (L ≠ PR_3), we studied the reaction of $[(cymene)RuCl(\mu\text{-}Cl)]_2$ with $[RuCl_2(cod)(NCCH_3)_2]$. This complex was chosen because the acetonitrile ligands could be expected to be labile. After reaction in refluxing acetone and crystallization from CH_2Cl_2/pentane, we were able to isolate the dimeric complex **6** (Scheme 3).



Scheme 3. Synthesis of complex **6**

Due to the reduced symmetry of **6** as compared to $[RuCl_2(cod)(NCCH_3)_2]$, four discrete signals due to the C atoms of the cyclooctadiene ligand are observed in its ^{13}C NMR spectrum ($CDCl_3$). Accordingly, two groups of signals are observed for the olefinic protons in the ^1H NMR spectrum. X-ray analysis of **6** reveals a structure similar to that of **5**, with the dppb ligand being substituted by a cod ligand (Figure 3). Again, the Ru−Cl bond length to the terminal chloro ligand (2.39 Å) is shorter than the Ru−Cl distances of the bridging chloro ligands (2.42−2.49 Å). The cyclooctadiene ligand shows the normal tub conformation with Ru−C bond lengths in the expected range.[17]

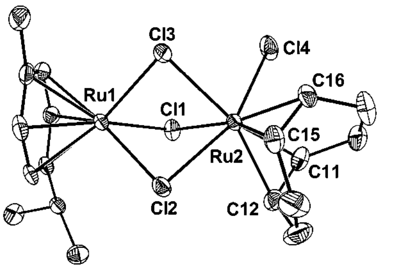


Figure 3. Molecular structure of **6** in the crystal; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Ru1−Cl1 2.441(1), Ru1−Cl2 2.422(1), Ru1−Cl3 2.441(1), Ru2−Cl1 2.482(1), Ru2−Cl2 2.454(1), Ru2−Cl3 2.485(1), Ru2−Cl4 2.388(1), Ru2−C11 2.177(4), Ru2−C12 2.185(4), Ru2−C15 2.174(4), Ru2−C16 2.181(4); Cl2−Ru1−Cl1 79.02(4), Cl4−Ru2−Cl2 158.06(4), Cl4−Ru2−Cl3 84.31(5), Cl2−Ru2−Cl3 78.54(4), Cl1−Ru2−Cl3 82.00(4), Ru1−Cl3−Ru2 83.53(3)

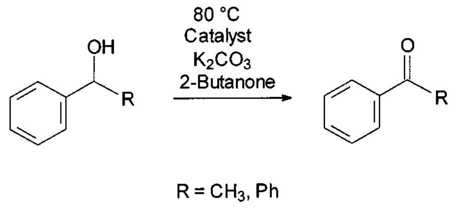
Catalytic Oxidations of Secondary Alcohols

Various methods are available for the oxidation of alcohols to carbonyl compounds. Especially appealing − both from an economic as well as environmental point of view − are transition metal catalyzed oxidations in which ketones act as both the solvent and the oxidant for the process. One of the most successful catalyst precursors for this Oppenauer-type[18] reaction is $[RuCl_2(PPh_3)_3]$. This was demonstrated by the group of Bäckvall. In the presence of K_2CO_3, hydrogen is catalytically transferred from secondary alcohols to acetone with high efficiency.[19] We have investigated the ability of the aforementioned dinuclear complexes to catalytically oxidize alcohols under conditions similar to those employed by Bäckvall. In a first series of experiments, we screened the reactivities of **1** and **3−6** in the oxidation of diphenylmethanol. Using 0.2 mol-% of the catalyst precursor, 2-butanone as the hydrogen acceptor, and K_2CO_3 as the base, we were able to obtain benzophenone in 22−94% yield (Table 1, Entries 1−5, Scheme 4). The heterobimetallic Cp^*Rh^{III} complex **3** displayed the highest activity. Subsequently, we tested the activities of the metal complexes used in our synthesis. All the half-sandwich complexes displayed activities comparable to that of $[RuCl_2(PPh_3)_3]$, but significantly lower than that of **3** (Table 1, Entries 6−10). The phosphane complexes **1** and **3−5** were also employed in the oxidation of 1-phenylethanol (Table 1, Entries 11−14). Again, the highest yield was obtained with complex **3**, followed by the (cymene)Ru^{II} complex **4**. With acetophenone as the substrate, initial turnover frequencies were determined. For all the dinuclear complexes, values in excess of 1000 h^{-1} were obtained, with a maximum of 3400 h^{-1} for the reactions with complex **3**.

Table 1. Catalytic oxidation of diphenylmethanol and 2-phenylethanol by 2-butanone; the reactions were performed in refluxing 2-butanone (2.00 mL) with 0.40 mmol of the substrate, the appropriate catalyst (0.80 μmol), and K_2CO_3 (0.40 mmol)

Entry	Complex	R	Time [h]	Yield [%][a]
1	**1**	Ph	3	92
2	**3**	Ph	3	94
3	**4**	Ph	3	29
4	**5**	Ph	3	25
5	**6**	Ph	3	22
6	$[(cymene)RuCl_2]_2$[b]	Ph	3	14
7	$[Cp^*RhCl_2]_2$ [b]	Ph	3	15
8	$[Cp^*IrCl_2]_2$ [b]	Ph	3	14
9	$[RuCl_2(PPh_3)_3]$	Ph	3	16
10	$[RuCl_2(dppb)(PPh_3)]$	Ph	3	4
11	**1**	CH_3	1	86
12	**3**	CH_3	1	99
13	**4**	CH_3	1	68
14	**5**	CH_3	1	70

[a] Determined by GC analysis. − [b] Substrate/metal = 500:1.



Scheme 4

In order to test the scope of the catalyst precursor **3**, oxidations of several other aromatic and aliphatic (cyclic and linear) alcohols have been carried out. With just 0.2 mol-% of **3**, good to excellent yields were obtained after 1 h (Table 2). Remarkably, even cyclohexanol, a substrate which is known to be problematic,[19] was converted into cyclohexanone in 85% yield within 1 h. With $[RuCl_2(PPh_3)_3]$ under otherwise identical conditions, only 5% of the product was obtained. Oxidation of the primary alcohol $PhCH_2OH$ was not possible with our catalyst system. Deactivation of the catalyst through the formation of carbonyl complexes is a possible explanation. In the oxidation of the unsaturated alcohol cyclohexenol, the isomer cyclohexanone was observed as a side product. Contrary to previous reports concerning reactions with $[RuCl_2(PPh_3)_3]$,[19a] the presence of a small amount of water (0.5%) reduces the activity of **3**. Although catalytic amounts of base are sufficient to initiate the reaction, larger quantities of K_2CO_3 are favorable because the base can bind residual water. No reaction was observed in the absence of base.

Table 2. Oxidation of secondary alcohols by 2-butanone in the presence of the heterobimetallic complex **3**; the reactions were performed as described in the Exp. Sect. with a substrate/catalyst ratio of 500:1

Entry	Substrate	Product	Yield [%][a]
1	1-indanol	1-indanone	> 99
2	1-tetralol	1-tetralone	97
3	cyclopentanol	cyclopentanone	95
4	cyclohexanol	cyclohexanone	85
5	cycloheptanol	cycloheptanone	99
6	2-octanol	2-octanone	86

[a] The yield was determined by GC analysis after 1 h.

The mechanism of this potentially very complicated reaction has still to be elucidated. Most probably, one or more hydrido complexes are formed through reaction of **3** with the deprotonated substrate. This kind of reaction has been described for $[Cp^*RhCl(\mu\text{-}Cl)]_2$[20] as well as for $[RuCl_2(PPh_3)_3]$.[6c] The hydrido complex(es) represent(s) the catalytically active species, being able to transfer hydrogen from the substrate to 2-butanone. Based on the results of our control experiments, which show that $[Cp^*RhCl(\mu\text{-}Cl)]_2$ and $[RuCl_2(PPh_3)_3]$ on their own are less active (Table 1, Entries 7 and 9), and the fact that $RuHX(PPh_3)_2$ (X = Cl, H) is electronically unsaturated,[21] it is reasonable to predict that di- or polynuclear complexes with chloro and/or hydrido bridges play an important role in the catalytic cycle.

Conclusions

We have shown that half-sandwich complexes of ruthenium, rhodium, and iridium can be used to stabilize $RuCl_2(PPh_3)_2$, a metal fragment with special importance in homogeneous catalysis. In the dinuclear complexes formed, the two metal centers are connected by three chloro bridges. With regard to future applications in organic synthesis, it should be emphasized that the synthesis of these complexes is fast and easy: they can be obtained in virtually 100% yield by reaction of commercially available half-sandwich complexes with **2**, which itself can be prepared in crystalline form simply by mixing $[RuCl_2(PPh_3)_3]$ with acetone. Half-sandwich complexes are also suited for stabilizing other $RuCl_2L_2$ fragments. This has been demonstrated by synthesizing complex **5** with a chelating phosphane ligand and complex **6** with a cyclooctadiene ligand. We assume that related complexes can be obtained in a similar fashion.

The heterobimetallic $Rh^{III}-Ru^{II}$ complex **3** represents one of the best catalyst precursors for the Oppenauer-type oxidation of simple secondary alcohols yet found. In the presence of 0.2 mol-% of **3** and a weak base, aromatic and aliphatic alcohols are converted into the corresponding ketones in good to excellent yield within 1 h. Side reactions are not generally observed.

We are currently exploring the potential of these types of bimetallic complexes to act as catalyst precursors for other reactions. Both metal fragments − the organometallic π-complex[22] as well as the $RuCl_2L_2$ fragment − are known to be essential constituents of catalysts for hydrogenations, the metathesis of olefins, and isomerization reactions, among others. We think that the combination of these two fragments within one molecule can give rise to new catalyst systems with superior characteristics (solubility, activity, selectivity). Further results will be presented in the near future.

Experimental Section

General Remarks: All reactions were performed under dry dinitrogen. The solvents were distilled from appropriate drying agents and stored under dinitrogen. 2-Butanone (> 99.7%) was obtained from Riedel-de Häen and degassed prior to use. The complexes $[RuCl_2(PPh_3)_3]$,[23] $[RuCl_2(PPh_3)(dppb)]$,[24] $[(cymene)RuCl(\mu\text{-}Cl)]_2$,[25] $[Cp^*MCl(\mu\text{-}Cl)]_2$ (M = Rh, Ir),[26] and $[RuCl_2(cod)(NCCH_3)_2]$[27] were prepared according to literature procedures. − NMR spectra were recorded with JEOL EX 400 or GSX 270 spectrometers using the residual protonated solvents as internal standards. − GC-MS analyses were performed with a CP-cyclodextrin-B-2,3,6-M-19 column (50 m) coupled to a Varian 3800 spectrometer.

2: $[RuCl_2(PPh_3)_3]$ (959 mg, 1.00 mmol) was suspended in acetone (60−500 mL) without stirring. After several days, red crystals had formed, which were isolated, washed with acetone (4 × 100 mL), and dried in a stream of dinitrogen. The yields (53−90%) and the reaction times (2−14 d) were found to depend on the amount of acetone. Large amounts of acetone give short reaction times but also reduce the yields. − $C_{39}H_{36}Cl_2OP_2Ru$ (754.6): calcd. C 62.07, H 4.81; found C 61.95, H 4.88.

Synthesis of Complexes 1, 3, and 4: A mixture of **2** (75.5 mg, 0.10 mmol) and the appropriate chloro-bridged complex (0.05 mmol) in CH_2Cl_2 (15 mL) was stirred until a clear solution had been obtained (1−2 h). After removal of the solvent under reduced pressure and drying in vacuo, the products were obtained in quantitative yields.

1: Red powder. − ^1H NMR (270 MHz, CD_2Cl_2): δ = 1.19 [d, ^3J = 7 Hz, 6 H, $CH(CH_3)_2$], 2.12 (s, 3 H, CH_3, cymene), 2.75 [s, ^3J = 7 Hz, 1 H, $CH(CH_3)_2$], 5.15 (d, ^3J = 11 Hz, 1 H, $CH{=}CH_2$), 5.22 (d, ^3J = 5 Hz, 2 H, CH, cymene), 5.38 (d, ^3J = 5 Hz, 2 H, CH, cymene), 7.00−7.30 (m, 30 H, Ph). − ^{13}C NMR (68 MHz, CD_2Cl_2): δ = 18.4, 22.0 (CH_3, cymene), 30.9 (CH, cymene), 78.4, 78.5 (CH, cymene), 95.3, 101.4 (C, cymene), 126.8−136.1 (Ph). − ^{31}P NMR (109 MHz, CD_2Cl_2): δ = 50.3. − $C_{46}H_{44}Cl_4P_2Ru_2\cdot 1/2CH_2Cl_2$ (1045.2): calcd. C 53.43, H 4.34; found C 53.59, H 4.25.

3: Red powder. − ^1H NMR (270 MHz, CD_2Cl_2): δ = 1.60 (s, 15 H, Cp*), 7.01−7.32 (m, 30 H, Ph). − ^{13}C NMR (68 MHz, CD_2Cl_2): δ = 9.1 (CH_3, Cp*), 93.7 (d, ^1J = 9 Hz, C, Cp*), 126.6−135.2 (Ph). − ^{31}P NMR (109 MHz, CD_2Cl_2): δ = 50.1. − $C_{46}H_{45}Cl_4P_2RhRu\cdot 1/4CH_2Cl_2$ (1026.8): calcd. C 54.10, H 4.47; found C 54.00, H 4.53.

4: Red powder. − ^1H NMR (270 MHz, CD_2Cl_2): δ = 1.56 (s, 15 H, Cp*), 7.02−7.35 (m, 30 H, Ph). − ^{13}C NMR (68 MHz, CD_2Cl_2): δ = 8.9 (CH_3, Cp*), 85.3 (C, Cp*), 126.5−136.1 (Ph). − ^{31}P NMR (109 MHz, CD_2Cl_2): δ = 52.1. − $C_{46}H_{45}Cl_4P_2RhRu\cdot 2/3CH_2Cl_2$ (1151.5): calcd. C 48.68, H 4.06; found C 48.50, H 4.15.

5: A solution of $RuCl_2(dppb)(PPh_3)$ (172 mg, 0.20 mmol) and $[(cymene)RuCl_2]_2$ (122 mg, 0.20 mmol) in acetone (25 mL) was heated under reflux. After 30 min, the heating was stopped and the solution was placed in a freezer (−20 °C). After 7 d, red crystals had formed, which were isolated and dried in a stream of dinitrogen. Yield: 109 mg (60%). − ^1H NMR (270 MHz, CD_2Cl_2): δ = 1.17 [d, ^3J = 7 Hz, 6 H, $CH(CH_3)_2$], 1.21−1.32 (m, 2 H, CH_2), 1.75−1.87 (m, 2 H, CH_2), 2.00−2.09 (m, 2 H, CH_2), 2.12 (s, 3 H, CH_3, cymene), 2.71 [s, ^3J = 7 Hz, 1 H, $CH(CH_3)_2$], 3.11−3.20 (m, 2 H, CH_2), 5.18 (d, ^3J = 6 Hz, 2 H, CH, cymene), 5.31 (d, ^3J = 6 Hz, 2 H, CH, cymene), 7.21−7.65 (m, 20 H, Ph). − ^{13}C NMR (68 MHz, CD_2Cl_2): δ = 18.4, 22.0, 22.6 (CH_2, dppb; CH_3, cymene), 29.8, 30.0, 30.3 (m, PCH_2), 30.9 (CH, cymene), 78.3, 78.5 (CH, cymene), 95.0, 101.0 (C, cymene), 127.0−140.7 (Ph). − ^{31}P NMR (109 MHz, CD_2Cl_2): δ = 54.4. − $C_{38}H_{42}Cl_4P_2Ru_2CH_3COCH_3$ (962.7): calcd. C 51.15, H 5.03; found C 51.20, H 5.05.

6: A mixture of $[RuCl_2(cod)(NCCH_3)_2]$ (38.0 mg, 0.10 mmol) and $[(cymene)RuCl(\mu\text{-}Cl)]_2$ (30.6 mg, 0.05 mmol) in acetone (10 mL) was heated under reflux for 1 h. After removal of the solvent under reduced pressure, the product was crystallized from CH_2Cl_2/hexane. Orange crystals, yield 49 mg (82%). − ^1H NMR (270 MHz, $CDCl_3$): δ = 1.39 [d, ^3J = 7 Hz, 6 H, $CH(CH_3)_2$], 1.72−1.81 (m, 4 H, CH_2, cod), 2.23−2.31 (m, 2 H, CH_2, cod), 2.32 (s, 3 H, CH_3, cymene), 2.44−2.50 (m, 2 H, CH_2, cod), 2.96 [s, ^3J = 7 Hz, 1 H, $CH(CH_3)_2$], 4.33−4.39 (m, 2 H, CH, cod), 4.44−4.50 (m, 2 H, CH, cod), 5.44 (d, ^3J = 6 Hz, 2 H, CH, cymene), 5.66 (d, ^3J = 6 Hz, 2 H, CH, cymene). − ^{13}C NMR (68 MHz, CD_2Cl_2): δ = 18.8, 22.5, 29.6, 29.9, 31.3 (CH_2, cod; CH, CH_3, cymene), 78.1, 79.6, 84.5, 84.9 (CH, cod + cymene), 97.2, 101.0 (C, cymene). − $C_{18}H_{26}Cl_4Ru_2$ (586.4): calcd. C 36.87, H 4.47; found C 36.87, H 4.43.

Crystal Structure Analyses: The structures of complexes **2** and **5** were determined with a Stoe IPDS. The structure of complex **6** was determined with an Enraf−Nonius diffractometer. Structure solution was performed by direct methods using SHELXS-97 or SHELXS-86.[28] The structures were refined by full-matrix least-squares techniques on F^2 (SHELXL-97, SHELXL-93).[28] For the hydrogen atoms, a riding model was employed. Complex **5** co-crystallized with pentane and dichloromethane. There are three molecules of CH_2CH_2 in the unit cell, the positions of two of which are only partially occupied (Table 3). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-144081 (**5**), -144082 (**2**), -144083 (**6**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-(0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

General Procedure for the Catalytic Oxidation of Secondary Alcohols: A suspension of K_2CO_3 (55.3 mg, 0.40 mmol) and the substrate (0.40 mmol) in 2-butanone (2.00 mL) was heated under reflux under dry dinitrogen. The reaction was initiated by addition of the catalyst (0.8 μmol), dissolved in CH_2Cl_2 (0.40 mL). After the time indicated, a sample (50 μL) was removed from the reaction vessel, quenched with acetone/acetic acid (3.5:1, 450 μL), and analyzed by capillary GC. The initial turnover frequency for the reduc-

Table 3. Crystallographic data for complexes **2**, **5**, and **6**

	2	**5**	**6**
Empirical formula	$C_{78}H_{72}Cl_4O_2P_4Ru_2$	$C_{83.4}H_{100.8}Cl_{12.8}P_4Ru_4$	$C_{18}H_{26}Cl_4Ru_2$
Molecular mass [g mol^{-1}]	1509.25	2085.26	586.33
Crystal size	0.15 × 0.12 × 0.06	0.23 × 0.05 × 0.04	0.43 × 0.37 × 0.53
Crystal system	monoclinic	triclinic	monoclinic
Space group	*Cc*	$P\bar{1}$	$P2_1/n$
a [Å]	25.4377(17)	16.1765(11)	10.4555(14)
b [Å]	12.2724(6)	17.8665(15)	10.487(2)
c [Å]	22.6572(14)	18.5778(18)	19.063(3)
α [°]	90	109.395(10)	90
β [°]	105.028(8)	94.293(10)	96.843(12)
γ [°]	90	116.366(8)	90
Volume [Å^3]	6831.3(7)	4377.9	2075.3(6)
Z	4	2	4
Density [g cm^{-3}]	1.467	1.582	1.877
Temperature [K]	200(3)	200(3)	295(2)
Absorption coefficient [mm^{-1}]	0.740	1.183	1.969
Θ range [°]	1.66 to 23.98	1.74 to 25.81	2.12 to 23.98
Index ranges	$-28 \le h \le 29$	$-18 \le h \le 18$	$-11 \le h \le 0$
	$-13 \le k \le 13$	$-21 \le k \le 21$	$0 \le k \le 11$
	$-25 \le l \le 25$	$-22 \le l \le 22$	$-21 \le l \le 21$
Reflections collected	18798	34346	3430
Independent reflections	9825 (R_{int} = 0.0509)	15738 (R_{int} = 0.0899)	3235 (R_{int} = 0.0145)
Absorption correction	numerical	numerical	semi-empirical
Max. and min. transmission	0.9581 and 0.9150	0.9732 and 0.9127	0.9984 and 0.8846
Data/restraints/parameters	8009/2/815	7735/2/898	3109/0/221
Goodness-of-fit on F^2	0.871	0.765	1.156
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0307$, $wR2 = 0.0589$	$R1 = 0.0456$, $wR2 = 0.0836$	$R1 = 0.0260$, $wR2 = 0.0817$
R indices (all data)	$R1 = 0.0442$, $wR2 = 0.0751$	$R1 = 0.1165$, $wR2 = 0.0968$	$R1 = 0.0270$, $wR2 = 0.0825$
Largest diff. peak/hole [eÅ^{-3}]	0.320/−0.511	2.018/−0.767	0.512/−0.527

tion of acetophenone was deduced from the time course of product formation over the first 10 min.

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