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Heterodinuclear Arene Ruthenium Complexes Containing a Glycine-Derived Phosphinoferrocene Carboxamide: Synthesis, Molecular Structure, Electrochemistry, and Catalytic Oxidation Activity in Aqueous Media

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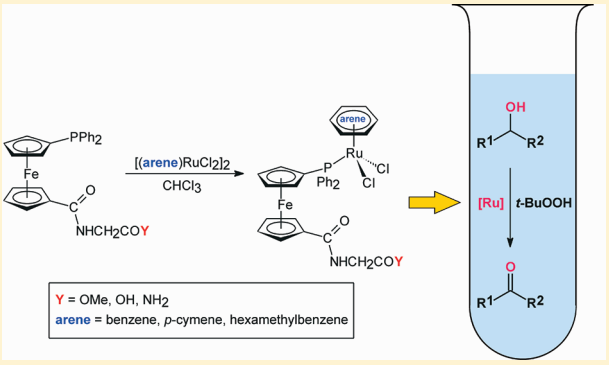
Supporting Information

ABSTRACT: Three series of heterodinuclear ruthenium−iron complexes have been synthesized from (η^6-arene)ruthenium dichloride dimers and phosphinoferrocene ligands containing glycine-based carboxamido substituents. The neutral complexes [(η^6-arene)RuCl$_2$(Ph$_2$PfcCONHCH$_2$CO$_2$Me-κP)] (**4**, arene = benzene (**a**), *p*-cymene (**b**), hexamethylbenzene (**c**); fc = ferrocene-1,1′-diyl) were obtained by the bridge cleavage reaction of [(η^6-arene)RuCl$_2$]$_2$ with Ph$_2$PfcCONHCH$_2$CO$_2$Me (**1**) in chloroform solution. The complex [(η^6-*p*-cymene)-RuCl$_2$(Ph$_2$PfcCONHCH$_2$CONH$_2$-κP)] (**6b**) was synthesized in the same way from Ph$_2$PfcCONHCH$_2$CONH$_2$ (**3**); the preparation of [(η^6-*p*-cymene)RuCl$_2$(Ph$_2$PfcCONHCH$_2$CO$_2$H-κP)] (**5b**), featuring the ferrocene ligand in the free acid form (**2**), failed due to side reactions and isolation problems. The salts [(η^6-arene)RuCl(MeCN)(**1**-κP)][PF$_6$] (**7a−c**) and [(η^6-arene)Ru(MeCN)$_2$(**1**-κP)][PF$_6$]$_2$ (**8a−c**) were prepared from **1** and the acetonitrile precursors [(η^6-arene)RuCl(MeCN)$_2$][PF$_6$] and from **4a−c** via halide removal with Ag[PF$_6$] in acetonitrile solution, respectively. Alternative synthetic routes to **7b** and **8b** were also studied. The compounds were fully characterized by elemental analysis, multinuclear NMR, IR, and electrospray ionization mass spectra, and their electrochemical properties were studied by cyclic voltammetry at a Pt-disk electrode. The single-crystal X-ray analyses of two representatives (**4b** and **8b**) revealed a pseudotetrahedral coordination geometry at the ruthenium centers and eclipsed conformations of the ferrocene moieties, with the substituents at the two cyclopentadienyl rings being anti with respect to each other. All complexes showed high activity for the catalytic oxidation of secondary alcohols with *tert*-butyl hydroperoxide to give ketones in aqueous media. The most active catalyst was obtained from the neutral *p*-cymene complex **4b**, showing a catalytic turnover frequency of 13 200 h^{-1} at room temperature for the oxidation of 1-phenylethanol at a substrate/catalyst ratio of 100 000.



INTRODUCTION

Ligands obtained by "conjugation" of phosphinocarboxylic acids with amino acids have received considerable attention in the recent past, owing to their rich coordination chemistry and manifold catalytic applications.[1,2] Indeed, these compounds represent attractive targets for ligand design, being synthesized readily in good yields by conventional amide coupling reactions and are thus accessible in many variants, differing in the overall structure and substitution patterns.

Stimulated by our investigation into the chemistry of 1′-(diphenylphosphino)ferrocene-1-carboxamides with simple[3] and functional substituents at the amide nitrogen (type **A** in Scheme 1; e.g., compounds bearing pyridyl,[4] hydroxyalkyl,[5] and sulfonatoalkyl[6] groups), we have recently turned also to analogous donors prepared from amino acids. So far, we have synthesized and catalytically tested several such ligands obtained from 1′-(diphenylphosphino)ferrocene-1-carboxylic acid (Hdpf) or its planar-chiral 1,2-isomer and from both achiral glycine (compounds **1−3** in Scheme 1)[7] and various chiral amino acids.[8] We have also demonstrated that these ligands are easily modified at their amide substituent. For instance, compound **1**, resulting from Hdpf and glycine methyl ester hydrochloride, was readily converted to the corresponding acid **2** (by hydrolysis) or amide **3** (by reaction with liquid ammonia).[7] These changes naturally affect both the coordination and physicochemical properties (e.g., solubility) of these donors and can be thus used to fine tune the catalytic performance of complexes prepared thereof.

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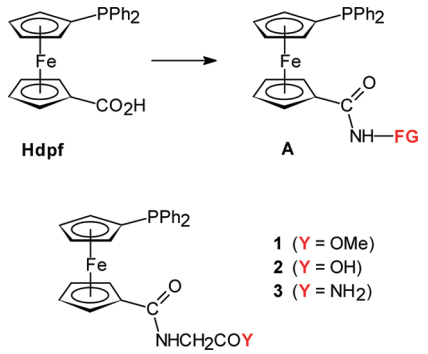
Scheme 1. Hdpf Derivatives



In the search for other potentially useful synthetic transformations in which Hdpf–amino acid conjugates could be used, we turned to transition-metal-catalyzed *oxidation* reactions. Phosphinoferrocene ligands have been used only rarely in such reactions, presumably due to their possible decomposition following oxidation of the ferrocene unit.[9] In this contribution, we describe the preparation, structural characterization, and electrochemistry of three series of (η^6-arene)Ru complexes with glycine-based amidophosphine ligands **1**–**3**. We also report the catalytic performance of these ruthenium–iron complexes in the selective oxidation of secondary alcohols with *tert*-butyl hydroperoxide to give the corresponding ketones.

RESULTS AND DISCUSSION

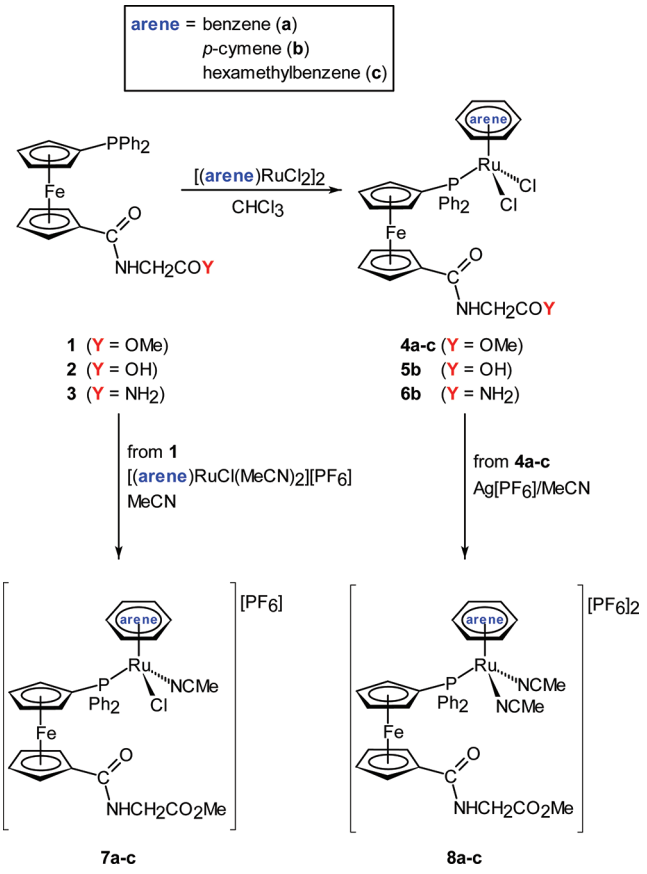
Synthesis and Structural Characterization of the Ruthenium–Iron Compounds. Three series of (η^6-arene)Ru complexes containing **1** as a P-monodentate ligand were prepared (Scheme 2); viz., the neutral complexes of the type [(η^6-arene)$RuCl_2$(**1**-κP)] as well as two series of cationic complexes resulting from the substitution of chloro by acetonitrile ligands, which were isolated as PF_6^- salts. The neutral complexes **4a**–**c** were obtained by a bridge cleavage reaction from the respective dimeric precursor [(η^6-arene)$RuCl_2$]$_2$ and **1** in chloroform. The related complex **6b** was synthesized similarly from the amide **3**. In contrast, attempts to prepare [(η^6-*p*-cymene)$RuCl_2$(**2**-κP)] (**5b**) from the free acid **2** were unsuccessful due to side reactions;[10] in our hands it was not possible to isolate **5b** (detected by NMR) from the reaction mixture.

Removal of the chloro ligands from **4a**–**c** with 2 equiv of Ag[PF_6] in acetonitrile produced the bis-acetonitrile complexes as hexafluorophosphate salts **8a**–**c**. The formally intermediary monoacetonitrile compounds **7a**–**c** were obtained by replacement of one acetonitrile ligand in the precursors [(η^6-arene)$RuCl(MeCN)_2$][PF_6] with a stoichiometric amount of ligand **1**.

Additional reactivity studies showed that the cationic complexes **7b** and **8b** are accessible either in a direct way from [(*p*-cymene)$RuCl(MeCN)_2$]$^+$ or [(*p*-cymene)$Ru(MeCN)_3$]$^{2+}$ via substitution of the acetonitrile ligands with **1** or, alternatively, by sequential removal of the chloro ligands from the dichlororuthenium complex **4b**. These interconversions are schematically shown in Scheme 3 and described in detail in the Supporting Information.

The compounds were characterized by combustion analyses, ^{1}H, ^{31}P{^{1}H}, and ^{19}F NMR spectroscopy, IR spectroscopy, and

Scheme 2. Preparation of Ruthenium–Iron Complexes 4–8



ESI mass spectrometry. The molecular structures of **4b** and **8b** were determined by single-crystal X-ray diffraction analysis.

The proton NMR spectra of **4a**–**c**, **5b**, and **8a**–**c** display characteristic signals of the arene ligand and four resonances attributable to the 1,1′-disubstituted ferrocene moiety. In the case of **7**, possessing a stereogenic Ru atom, the originally degenerate signals become diastereotopic and anisochronic. For instance, four CH resonances of the cymene CH groups and eight signals for the ferrocene protons are seen in the ^{1}H NMR spectrum of **7b**. The spectra further comprise signals due to the glycine pendant, namely the singlet of the terminal methyl group at δ_H ca. 3.7–3.8 and NH-coupled ($^3J_{HH} \approx 6$ Hz) doublet of the methylene group at δ_H 4.0–4.1. The spectrum of **6b** shows the expected three signals for the nonequivalent NH protons. The ^{31}P{^{1}H} NMR spectra of neutral complexes **4a**–**c** and **5b** display one singlet resonance in the range δ_P 15–19. This signal shifts to lower fields in the spectra of mono- and dicationic complexes (**7a**–**c**, δ_P 28–30; **8a**–**c**, δ_P 33–35 ppm). The presence of the hexafluorophosphate ion is manifested via a characteristic septet in the ^{31}P NMR spectrum (δ_P −145) and a doublet in the ^{19}F NMR spectrum (δ_F −73; $^1J_{PF}$ = 706 Hz).

The presence of amide and ester groups are clearly reflected in IR spectra showing intense bands due to ν_{NH} (ca. 3375 cm^{-1}), $\nu_{C=O}$ (1747–1751 cm^{-1}), amide I (1638–1653 cm^{-1}), and amide II (1530–1553 cm^{-1}) vibrations. The ester band is missing from the IR spectrum of **5b**, which on the other hand shows further bands due to the secondary and terminal primary amide groups. IR spectra of cationic complexes **7a**–**c** and **8a**–**c** further indicate the presence of coordinated MeCN ($\nu_{C\equiv N}$ 2293–2330 cm^{-1}) and the PF_6^- counterion (a strong band at 835–847 cm^{-1}). Positive-ion electrospray ionization (ESI)

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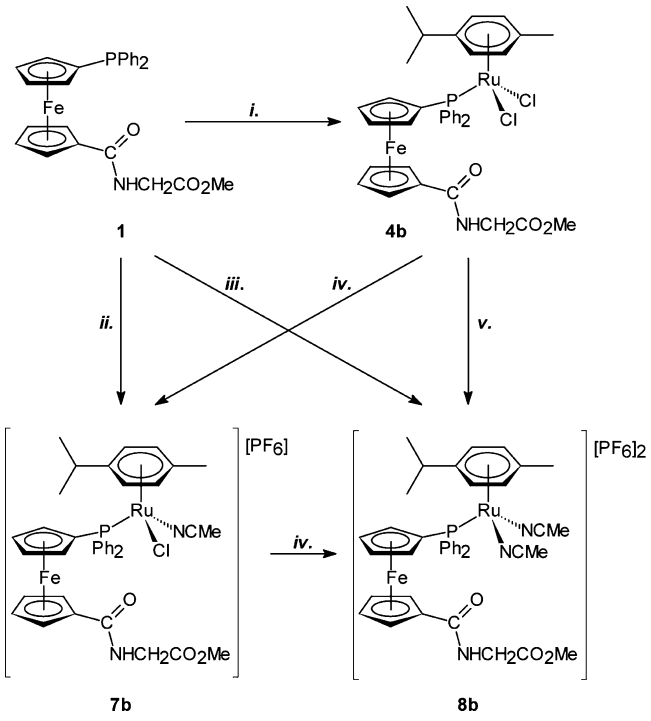
Scheme 3. Mutual Interconversions and Alternative Preparations of (η^6-*p*-cymene)ruthenium(II) Complexes with Ligand 1[a]



[a]Legend: (i) $[(p\text{-cymene})RuCl_2]_2$; (ii) $[(p\text{-cymene})RuCl(MeCN)_2][PF_6]$; (iii) $[(p\text{-cymene})Ru(MeCN)_3][PF_6]_2$; (iv) $Ag[PF_6]$; (v) 2 $Ag[PF_6]$. Reaction (i) was carried out in $CHCl_3$. All other reactions were performed in acetonitrile. For a complete description of the experiments, see the Supporting Information.

mass spectra of the neutral complexes **4a–c** and **5b** show ions corresponding to $[M + Na]^+$ or $[M - Cl]^+$. The spectra of the monocationic complexes **7a–c** display ions resulting via elimination of acetonitrile from their cations ($[M - MeCN - PF_6]^+$), while **8a–c** give rise to ions of the type $[(arene)Ru(\mathbf{1} - H)]^+$ or $[M - PF_6]^+$.

Description of the Crystal Structures. Single crystals suitable for X-ray diffraction analysis were obtained from diffusion of diethyl ether into a solution in methanol (**4b**·$2CH_3OH$) or acetonitrile (**8b**). Molecular structures of the complex molecule in the solvate **4b**·$2CH_3OH$ and the cation in the structure of **8b** are presented in Figure 1. Selected geometric data are given in Table 1.

The overall structures of both complex species are rather similar: the axis of the cymene ligand is oriented roughly parallel to the vector connecting the simple ligands (Cl1/Cl2 or N2/N3), and the arene ring is practically parallel to the basal plane of the three-legged piano-stool structure.[11] The ferrocene units are rotated with respect to the (η^6-*p*-cymene)Ru^{II} unit, as evidenced by the dihedral angles of planes of the Ru-bound arene and the phosphinylated cyclopentadienyl rings being 79.2(3)° for **4b**·$2CH_3OH$ and 69.2(4)° for **8b**. Notably, the Cg3–Ru1–donor angles (see Table 1 for defninitions) in both compounds are rather similar (124.95(9)–130.37(9)° for **4b**·$2CH_3OH$, 126.0(2)–129.7(2)° for **8b**), which rules out any significant deformation of the coordination sphere around Ru resulting from different steric demands of the two-electron donors (Cl and CH_3CN vs the relatively bulkier phosphine). Otherwise, the Ru–donor distances and the overall geometry are unexceptional and compare well with the data reported previously for [(η^6-*p*-cymene)$RuCl_2$(Hdpf-κP)][12] and [(η^6-benzene)$Ru(MeCN)_2(PPh_3)](CF_3SO_3)_2$.[13]

The geometry of coordinated **1** does not differ much from that found for free $Ph_2PfcCONHCH_2CO_2Bu$-*t*.[7] The 1,1′-disubstituted ferrocene moieties in **4b**·$2CH_3OH$ and **8b** assume

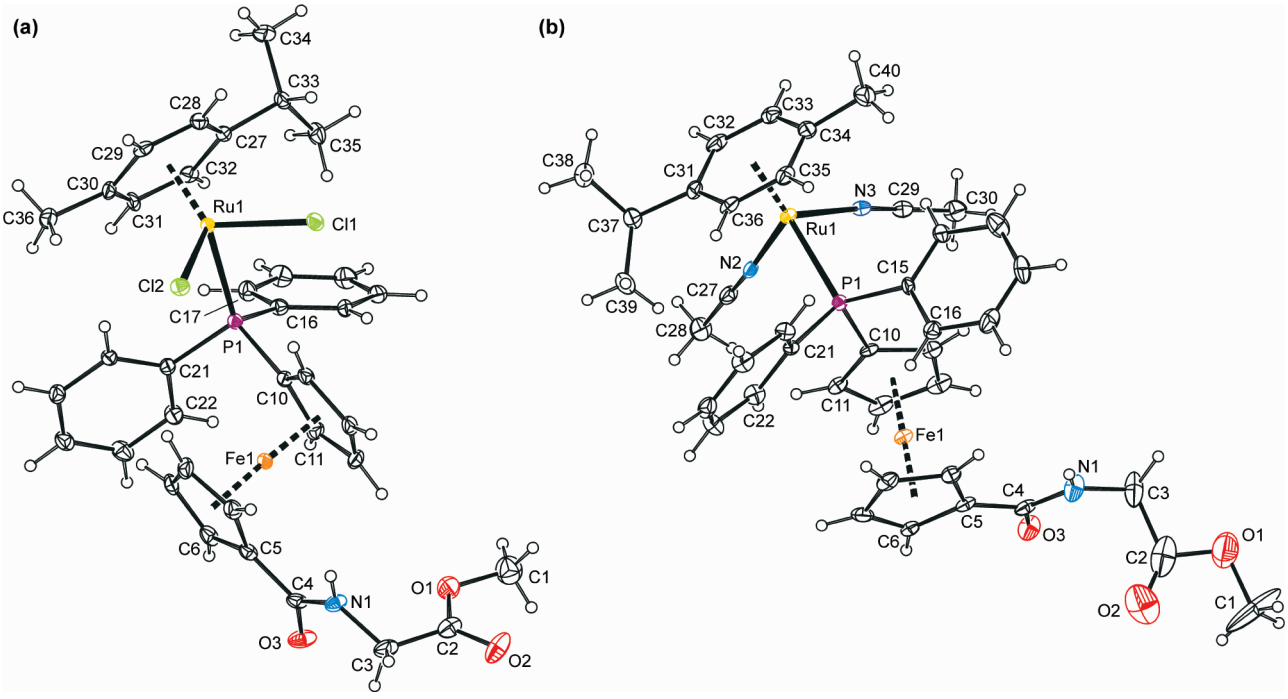


Figure 1. Views of (a) the complex molecule in **4b**·$2CH_3OH$ and (b) the cation in the structure of compound **8b**. Displacement ellipsoids correspond to the 30% probability level.

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Table 1. Selected Distances (Å) and Angles (deg) for Compounds 4b·2CH_3OH and 8b[a]

param	4b·2CH_3OH (X = Cl1, Z = Cl2)	8b[b] (X = N2, Z = N3)
Ru1−P1	2.380(1)	2.369(2)
Ru1−X	2.422(1)	2.062(6)
Ru1−Z	2.431(1)	2.056(6)
Ru−Cg3	1.718(2)	1.731(3)
P1−Ru1−X	86.75(5)	88.9(2)
P1−Ru1−Z	87.65(5)	84.8(2)
X−Ru1−Z	88.99(5)	84.9(2)
Fe1−Cg1	1.654(3)	1.656(4)
Fe1−Cg2	1.647(3)	1.654(4)
∠Cp1,Cp2	3.8(4)	3.2(5)
τ	156	137
φ	9.2(7)	8(1)
C4−O3	1.238(7)	1.229(9)
C4−N1	1.343(8)	1.339(9)
O3−C4−N1	121.1(6)	122.4(7)
C2−O1	1.326(8)	1.40(2)
C2−O2	1.215(8)	1.24(2)
O1−C2−O2	123.6(6)	122(1)

[a]Definitions: Cp1 = C(5−9), Cp2 = C(10−14), arene = benzene ring of the π-coordinated *p*-cymene (i.e., C(27−32) for **4b**, and C(31−36) for **8b**). Cg1, Cg2, and Cg3 denote the centroids of the Cp1, Cp2, and arene rings, respectively. τ = torsion angle C5−Cg1−Cg2−C10. φ = dihedral angle subtended by the plane Cp1 and the amide unit [C4, O3, N1]. [b]Further data: N2−C27 = 1.14(1) Å, N2−C27−C28 = 178.9(9)°, N3−C29 = 1.144(9) Å, N3−C29−C30 = 179.1(7)°.

intermediate conformations close to anti-eclipsed (compare the τ angles in Table 1 with the ideal value of 144°) and exert regular geometries with tilt angles of ca. 3−4° and individual Fe−C distances falling into narrow ranges (2.036(6)−2.061(6) and 2.033(8)−2.066(9) Å for 4b·2CH_3OH and **8b**, respectively). The planes of the amide moieties are rotated only by ca. 8−9° from the planes of their parent cyclopentadienyl rings (Cp1), and the whole amido-ester pendants extend away from the ferrocene and the (η^6-arene)Ru units.

Electrochemistry. The electrochemical properties of complexes **4a−c**, **5b**, **7a−c**, and **8a−c** were studied by cyclic voltammetry at a platinum-disk electrode. The measurements were performed on ca. 0.5 mM acetonitrile solutions containing 0.1 M [Bu_4N][PF_6] as the supporting electrolyte using ferrocene/ferrocenium as an internal reference. The pertinent data are summarized in Table 2.

When the external potential is increased in cyclic voltammetry, complexes **4a−c** undergo first a reversible one-electron redox change centered very likely at the ferrocene unit (Figure 2).[14] The separation of the anodic and cathodic peaks in cyclic voltammograms of these compounds was ca. 70−75 mV, similar to that of ferrocene/ferrocenium under the same experimental conditions. The ratios of the anodic and cathodic peak currents were close to unity, and the peak currents of this wave increased with the square root of the scan rate, indicating that the redox process is controlled by diffusion. Because of electron density transfer upon coordination, the redox potentials were more positive than that of free ligand **1** ($E^{\circ\prime}$ = 0.26 V in CH_2Cl_2).[7] Furthermore, the potentials decreased upon increasing the number of alkyl substituents at the Ru-bound arene ligand (i.e., with increasing donor ability of the η^6-arene donor).

A second redox event in **4a−c** observed at higher potentials is electrochemically irreversible and multielectron in nature

Table 2. Summary of Electrochemical Data for 4a−c, 5b, 7a−c, and 8a−c[a]

compd	$E^{\circ\prime}(Fe^{II/III})$ (V)	E_{pa}(Ru) (V)
4a	0.315	0.935
4b	0.285	0.850
4c[b]	0.245	0.710
5b	0.260	0.850
7a	0.430	n.d.
7b	0.410	n.d.
7c	0.385	n.d.
8a	0.540	n.d.
8b	0.530	n.d.
8c	0.510	n.d.

[a]The potentials are quoted relative to ferrocene/ferrocenium. $E^{\circ\prime}$ = $^1/_2(E_{pa} + E_{pc})$, where E_{pa} (E_{pc}) is the anodic (cathodic) peak potential in cyclic voltammetry. n.d. = not determined. [b]This compound shows a more complicated redox response (see text).

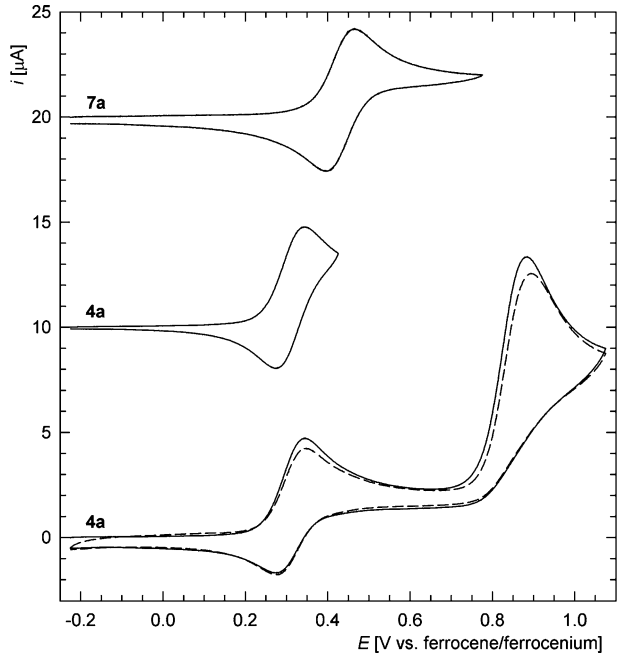

Figure 2. Cyclic voltammograms of complexes **4a** (full and partial) and **7a**, as recorded at a Pt-disk electrode on dichloromethane solutions (scan rate 100 mV s^{-1}). For clarity, the second scan is shown by a dashed line (for the full voltammogram of **4a**) and the voltammograms are shifted by +10 and +20 μA to avoid overlaps.

(Figure 2). The anodic peak potential (E_{pa}) of the second wave decreased significantly with an increasing number of arene substituents, suggesting the second redox change to occur predominantly at the (η^6-arene)Ru moiety. In the case of **4c**, an additional pair of redox waves was seen between the redox waves, probably due to adsorption. On the other hand, the redox response of compound **5b** did not differ from that of **4b**: the first wave appeared shifted slightly to lower potentials, while the redox potential of the second oxidation remained the same, which supports the assignment of the redox processes.

Replacement of the anionic chloro ligands by the neutral solvent molecules as in complexes **7** and **8** produces positively charged species, which could be expected to be more difficult to oxidize. Indeed, the cyclic voltammograms of **7a−c** displayed only one electrochemically reversible redox wave, attributable to the ferrocene/ferrocenium couple shifted to higher

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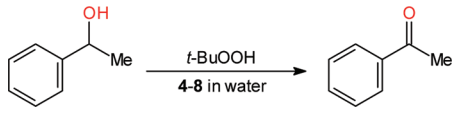
potentials as compared with that in the respective complexes **4a−c** (Figure 2). As for the parent neutral complexes, the compounds bearing more alkylated arene ligands became oxidized more easily ($E^{o\prime}$: **7c** < **7b** < **7a**). In the case of **8a−c**, this redox wave was shifted even further but was much less affected by the substituents at the arene ring. The second oxidations of **7** and **8** were probably located outside the accessible potential range.

Catalytic Reactions. Metal-catalyzed oxidation of alcohols to give carbonyl compounds such as aldehydes, ketones, and carboxylic acids is an important transformation both for organic synthesis and for industrial manufacturing.[15] There are many reports concerning this reaction using molecular oxygen[16] and hydrogen peroxide[17] as oxidants, the problem very often being the activity and selectivity of the catalyst. As far as this reaction in aqueous media is concerned, the oxidation of alcohols with H_2O_2 under phase-transfer conditions has been proposed.[18] Noyori reported a combined system composed of Na_2WO_4 and $[CH_3(n\text{-}C_8H_{17})_3N][HSO_4]$ as a phase-transfer catalyst, which efficiently catalyzes the oxidation of alcohols to the corresponding carbonyl compounds with high yields.[19] Trakarnpruk[20] and Punniyamurthy[21] compared the oxidation activity of hydrogen peroxide and *tert*-butyl hydroperoxide, another cheap and easy to use peroxide. A number of catalysts for the use of *t*-BuOOH have been reported to date.[22] Watanabe[23] and Muharashi[24] used the ruthenium complex $[RuCl_2(PPh_3)_3]$, which catalyzes the oxidation with high conversion (>92%). Recently, Singh used arene ruthenium complexes of the type $[(\eta^6\text{-arene})RuCl(L)][PF_6]$ (arene = *p*-cymene, benzene; L = *N*-[2-(arylchalcogeno)ethyl]morpholines with aryl = Ph, 2-pyridyl (for S), Ph (for Se), 4-$MeOC_6H_4$ (for Te)) as catalysts for alcohol oxidation, using *N*-methylmorpholine *N*-oxide (NMO), *t*-BuOOH, $NaIO_4$, and NaOCl as the oxidants.[25] We recently reported on the use of ruthenium arene bis-saccharinato complexes as alcohol oxidation catalysts that work efficiently in aqueous solution.[26]

All ruthenium−iron compounds reported above were tested as defined precatalysts in the oxidation of secondary alcohols to ketones. Complex **4b** obtained in a straightforward manner from the most easily accessible and cheapest Ru precursor was tested first in the oxidation of 1-phenylethanol as a model substrate with *t*-BuOOH in pure water (Scheme 4; for complete results in a tabulated form, see the Supporting Information, Table S1). Indeed, the oxidation reaction in the presence of 0.1 mol % of **4b** proceeded cleanly to produce acetophenone with complete conversion within 3 h (at room temperature). When the catalyst amount was lowered to 0.01 mol %, the conversion achieved in 3 h was only 83% but the reaction reached completion within 5 h. Decreasing the catalyst loading further to 0.001 mol % expectedly decreased the reaction rate (30% and 66% conversion in 3 and 5 h, respectively). Even in this case, however, complete conversion to acetophenone was achieved in 24 h. No reaction was seen without the Ru complex.

Scheme 4. Oxidation of 1-Phenylethanol to Acetophenone



A possible influence of the catalyst structure and reaction conditions on the course of the oxidation process was studied next. The results obtained with all defined (η^6-arene)Ru complexes in the model oxidation reaction at a substrate to catalyst ratio of 100 000:1, summarized in Table 3, clearly show the superior performance of compound **4b** at short reaction times. Only slightly worse results were obtained with the monocationic complexes **7a,c**. On the other hand, all catalysts tested gave complete or practically complete conversions in 24 h. This observation may indicate that the differences in performance observed at relatively shorter reaction times could reflect the ease of conversion of the defined precatalysts into the catalytically active species, presumably an aqua complex. This assumption is supported by our previous studies[25] and, indirectly, also by the observed dependence of turnover number on the pH of the reaction mixture (Figure 3). The best results were obtained at pH ca. 5.5−7.0. The aquation reaction, representing the likely catalyst activation step, is probably hindered at lower pH, while reactions at higher pH can lead to hydroxo complexes.[27] Otherwise, however, the

Table 3. Catalytic Activity of Complexes 4a−c, 6b, 7a−c, and 8a−c in the Oxidation of 1-Phenylethanol with *t*-BuOOH[a]

entry	cat.	conversn[b] after 5 h/24 h (%)	TON[c] after 24 h	TOF[d] after 5 h (h^{-1})
1	**4a**	30/99	99 000	6 000
2	**4b**	66/100	100 000	13 200
3	**4c**	45/100	100 000	9 000
4	**6b**	41/99	99 000	8 200
5	**7a**	61/100	100 000	12 200
6	**7b**	53/99	99 000	10 600
7	**7c**	61/100	100 000	12 200
8	**8a**	35/100	100 000	7 000
9	**8b**	38/99	99 000	7 600
10	**8c**	28/100	100 000	5 600
11	none	0/0	0	0

[a]Reaction conditions: alcohol (1.0 mmol) and *t*-BuOOH (4.0 mmol) in 4 mL of water, substrate/catalyst = 100 000, room temperature, reaction time 5 or 24 h. [b]Determined by ^{1}H NMR spectroscopy. [c]Turnover number: mol product/mol catalyst − after 24 h. [d]Turnover frequency: mol product/(mol catalyst × reaction time) − after 5 h.

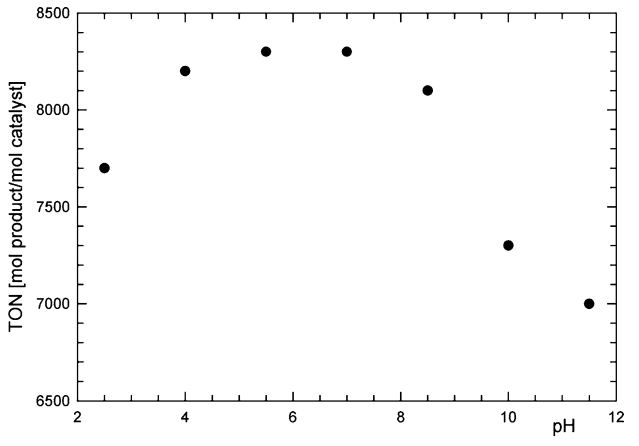


Figure 3. pH dependence of the turnover number (TON) for oxidation of 1-phenylethanol with *t*-BuOOH mediated by complex **4b** (0.01 mol %) at room temperature after 3 h. For tabulated results, see the Supporting Information (Table S1).

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reaction proceeded with no significant induction period and does not depart much from the exponential dependence expected for (pseudo) first-order kinetics (Figure 4).

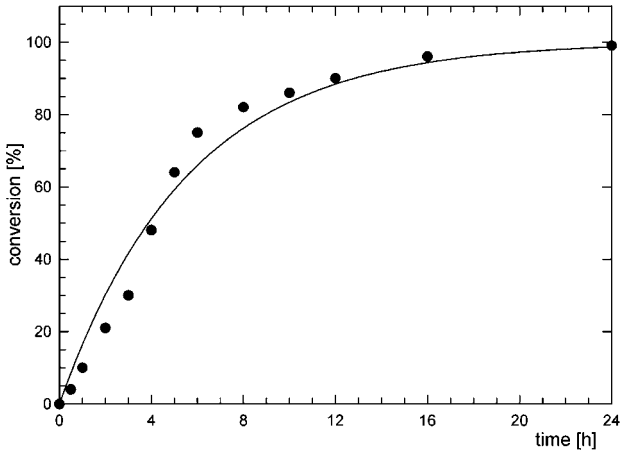

Figure 4. Kinetic profile for oxidation of 1-phenylethanol with *t*-BuOOH mediated by complex **4b** (0.01 mol %) at room temperature. The solid line represents an ideal kinetic fit: conversion = $a(1 - \exp[-bt])$. Parameters of the fit: a = 100(5)%, b = 0.18(2) h^{-1}, R^2 = 0.973.

Upon replacing pure water as the reaction mixture with organic solvents (hexane, diethyl ether, toluene, dichloromethane) or their biphasic aqueous mixtures, the oxidation reaction became considerably slower and did not reach completion even after 24 h (with 0.001 mol % catalyst; see the Supporting Information, Table S3). Also, when *t*-BuOOH was replaced with sodium perchlorate or sodium periodate (4 equiv), the conversions dropped to 9 and 62%, respectively, after 3 h (Supporting Information, Table S1). Other oxidants tested (aqueous hydrogen peroxide, benzoyl peroxide, 3-chloroperoxybenozic acid, oxone, or *N*-methylmorpholine *N*-oxide; 4 equiv vs the substrate) resulted in conversions not exceeding 3%. Bubbling air through the reaction mixture also did not induce any oxidation over 3 h.

A survey of various substrates (Table 4) showed that complex **4a** at 0.001 mol % loading promotes efficiently and cleanly the oxidation of 1-phenylethanol derivatives substituted at the benzene ring (entries 2−8), the exception being the 4-methoxyphenyl and 2-bromophenyl derivatives. The naphthyl analogue diphenylmethanol and even cyclic secondary alcohols with fused benzene rings were also efficiently oxidized (entries 9 and 11−13). On the other hand, 1-cyclohexylethanol and aliphatic secondary alcohols (entries 10, 14, and 15) gave only moderate conversions.

Water is the best reaction medium for this catalytic reaction, and the neutral dichloro complexes are more active than their monocationic monochloro acetonitrile and dicationic bis-(acetontrile) counterparts. Together with a pronounced pH dependence of the reaction course, this suggests that aquation of the chloro ligands plays an important role and that an aqua complex may be the real entry to the catalytic cycle. A mechanism based on this observation, in accordance with our earlier findings,[25] is shown in Scheme 5. Since we did not detect any oxoruthenium(IV) intermediates during our catalytic reactions, this mechanistic scheme remains only a plausible working hypothesis. The involvement of Ru−OOH species formed in situ (probably via an intermediate Ru aqua complex) cannot be ruled out at this point (see alternative route in Scheme 5).[28]

CONCLUSION

Heterobimetallic Fe^{II}−Ru^{II} complexes **4**−**8** are easily prepared from the common (η^6-arene)Ru^{II} precursors and phosphinoferrocene carboxamides with amino acid pendant chains, either in a direct way or in a convergent manner. Electrochemical studies revealed electronic communication between the $Ru^{II/III}$ and $Fe^{II/III}$ redox centers present in these compounds, typically manifested through changes in the redox potentials of both redox couples observed upon modification of only one of them. The stable compounds **4**−**8** give rise to highly active catalysts for the Ru-catalyzed oxidation of secondary alcohols to ketones. The oxidations are advantageously performed in water at room temperature and proceed cleanly and rapidly even at catalyst to substrate ratios as low as 1:100 000. Surprisingly, the presence of oxidation-sensitive ferrocene-based ligands does not seem to

Table 4. Oxidation of Various Secondary Alcohols in the Presence of Catalyst 4b[a]

entry	substrate	product	conversn[b] after 5 h/24 h (%)	isolated yield after 24 h (%)
1	1-phenylethanol	acetophenone	66/100	93
2	1-(4-fluorophenyl)ethanol	4′-fluoroacetophenone	46/99	92
3	1-(4-chlorophenyl)ethanol	4′-chloroacetophenone	53/100	90
4	1-(4-bromophenyl)ethanol	4′-bromoacetophenone	67/100	91
5	1-(4-methylphenyl)ethanol	4′-methylacetophenone	62/99	90
6	1-(4-methoxyphenyl)ethanol	4′-methoxyacetophenone	44/70	n.d.
7	1-(3-bromophenyl)ethanol	3′-bromoacetophenone	47/99	92
8	1-(2-bromophenyl)ethanol	2′-bromoacetophenone	8/35	n.d.
9	1-(2-naphthyl)ethanol	2′-acetonaphthone	53/100	91
10	1-cyclohexylethanol	hexahydroacetophenone	13/36	n.d.
11	diphenylmethanol	benzophenone	77/100	94
12	1-indanol	1-indanone	67/99	90
13	1-tetralol	1-tetralone	61/99	89
14	cyclohexanol	cyclohexanone	14/55	n.d.
15	2-butanol	2-butanone	8/29	n.d.

[a]Reaction conditions: alcohol (1.0 mmol) and *t*-BuOOH (4.0 mmol) in 4 mL of water, substrate/catalyst =100 000, room temperature, reaction time 5 or 24 h. [b]Determined by ^{1}H NMR spectroscopy.

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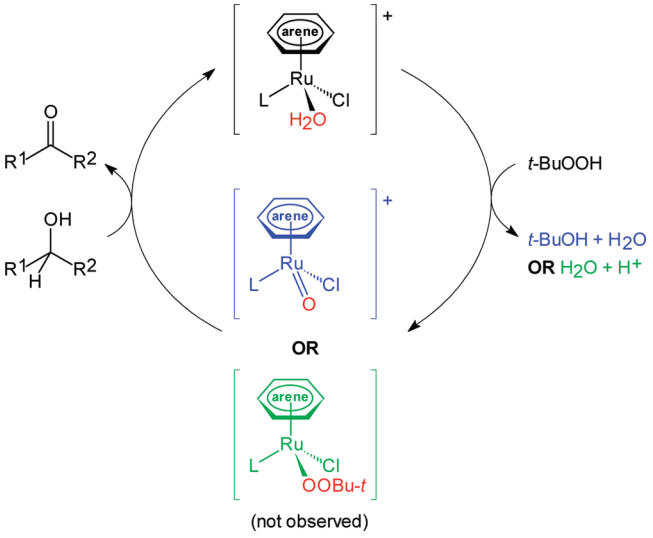
Scheme 5. Plausible Mechanistic Alternatives for the Ru-Catalyzed Oxidation of Alcohols with Peroxides[a]



[a]L is the P-coordinated amidophosphine **1**.

impose any limitations on the catalyst stability and performance.

EXPERIMENTAL SECTION

Materials and Methods. All (η^6-arene)Ru complexes were synthesized under a nitrogen atmosphere and with the exclusion of direct daylight. No such precautions were applied to the catalytic tests. The compounds $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = benzene, *p*-cymene),[29] $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$,[30] and $[(\eta^6\text{-arene})Ru(MeCN)_2Cl][PF_6]$[31] and ligands $Ph_2PfcC(O)NHCH_2COY$ (Y = OMe (**1**), OH (**2**), NH_2 (**3**))[7] were prepared according to the literature procedures. Solvents used in the syntheses and catalytic experiments were dried by standing over appropriate drying agents and distilled under nitrogen (dichloromethane, chloroform, and acetonitrile with CaH_2; hexane, diethyl ether, and toluene over sodium metal). Other chemicals and solvents used for crystallizations and in chromatography were used without further purification.

NMR spectra were recorded on a Bruker 400 MHz spectrometer (^{1}H, 400.13 MHz; ^{31}P, 161.98 MHz; ^{19}F, 376.50 MHz) at 296 K unless noted otherwise. Chemical shifts (δ/ppm) are given relative to the residual peak of the solvent (^{1}H; CD_3CN, δ_H = 1.94; $CDCl_3$, δ_H = 7.26), to 85% aqueous H_3PO_4 (^{31}P) or to neat $CFCl_3$ (^{19}F). Infrared spectra were recorded on KBr pellets with a Perkin–Elmer FTIR 1720-X spectrometer. Electrospray ionization (ESI) mass spectra were obtained in positive-ion mode with an LCQ Finnigan mass spectrometer.

Electrochemical measurements were performed with a computer-controlled multipurpose μAUTOLAB III potentiostat (Eco Chemie) at room temperature using a standard three-electrode cell equipped with a platinum-disk (AUTOLAB RDE, 3 mm diameter) working electrode, platinum-sheet auxiliary electrode, and double-junction Ag/AgCl (3 M KCl) reference electrode. Samples were dissolved in acetonitrile (Sigma-Aldrich, absolute) to give a solution containing ca. 0.5 mM of the analyte and 0.1 M $[Bu_4N][PF_6]$ (Fluka, purissimum for electrochemistry). The solutions were deaerated by bubbling with argon before the measurements and then kept under an argon blanket. The potentials are given relative to ferrocene/ferrocenium reference. The redox potential of the ferrocene/ferrocenium couple was 0.425 V vs Ag/AgCl (3 M KCl).

General Procedure for the Synthesis of Complexes [(η^6-arene)RuCl$_2$(1-κ*P*)] (4). A solution of ligand **1** (1.0 equiv) in $CHCl_3$ (5 mL per 0.2 mmol of the ligand) was added to the solid dimer $[(\eta^6\text{-arene})RuCl_2]_2$ (0.5 equiv). After the mixture was stirred at room temperature for 3 h, the solvent was evaporated under vacuum and the residue was purified by column chromatography on silica gel using chloroform/acetone (5/1 v/v) as the eluent.

Complex ***4a***. Starting from **1** (194 mg, 0.4 mmol) and $[(\eta^6\text{-benzene})RuCl_2]_2$ (100 mg, 0.2 mmol), the general procedure afforded **4a** as an orange foam. Yield: 274 mg (84%). ^{1}H NMR ($CDCl_3$, 50 °C): δ 3.36 (br s, 2 H, fc), 3.82 (s, 3 H, OMe), 4.13 (d, $^3J_{HH}$ = 6.1 Hz, 2 H, NHC*H*$_2$), 4.59 (br s, 2 H, fc), 4.69 (unresolved q, 2 H, fc), 4.72 (vt, 2 H, fc), 5.32 (s, 6 H, η^6-C_6H_6), 7.34–7.46 (m, 6 H, PPh_2), 7.70–7.82 (m, 4 H, PPh_2), 7.83 (t, $^3J_{HH}$ = 6.2 Hz, 1 H, N*H*CH$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, 50 °C): δ 15.2 (s). IR (KBr): ν_{NH} 3306 m, ν_{CO} 1747 vs, amide I 1651 vs, amide II 1553 vs cm^{-1}. MS (ESI+): *m*/*z* 758 ([M + Na]$^+$), 700 ([M – Cl]$^+$). Anal. Calcd for $C_{32}H_{30}NO_3PCl_2FeRu\cdot0.65CHCl_3$: C, 48.24; H, 3.80; N, 1.72. Found: C, 48.29; H, 3.80; N, 1.62.

Complex ***4b***. Starting from **1** (146 mg, 0.3 mmol) and $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (92 mg, 0.15 mmol), the general procedure gave **4b** as an orange solid. Yield: 225 mg (94%). ^{1}H NMR ($CDCl_3$): δ 0.99 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, CH*Me*$_2$), 1.70 (s, 3 H, η^6-C_6H_4*Me*), 2.44 (sept, $^3J_{HH}$ = 6.9 Hz, 1 H, *CH*Me$_2$), 3.27 (br s, 2 H, fc), 3.78 (s, 3 H, OMe), 4.09 (d, $^3J_{HH}$ = 6.1 Hz, 2 H, NHC*H*$_2$), 4.49 (vt, 2 H, fc), 4.55 (br s, 2 H, fc), 4.58 (unresolved q, 2 H, fc), 5.12 (d, $^3J_{HH}$ = 5.5 Hz, 2 H, η^6-C_6H_4), 5.19 (d, $^3J_{HH}$ = 6.1 Hz, 2 H, η^6-C_6H_4), 7.36–7.46 (m, 6 H, PPh_2), 7.59 (t, $^3J_{HH}$ = 6.0 Hz, 1 H, N*H*CH$_2$), 7.75–7.85 (m, 4 H, PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 17.2 (s). IR (KBr): ν_{NH} 3315 m, ν_{CO} 1750 vs, amide I 1648 vs, amide II 1530 vs cm^{-1}. MS (ESI+): *m*/*z* 814 ([M + Na]$^+$), 756 ([M – Cl]$^+$). Anal. Calcd for $C_{36}H_{38}NO_3PCl_2FeRu\cdot0.05CHCl_3$: C, 54.30; H, 4.81; N, 1.76. Found: C, 54.20; H, 4.78; N, 1.66.

Complex ***4c***. Starting with ligand **1** (146 mg, 0.3 mmol) and $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ (100 mg, 0.15 mmol), the general procedure gave **4c** as a red solid. Yield: 228 mg (91%). ^{1}H NMR ($CDCl_3$, 50 °C): δ 1.67 (s, 18 H, η^6-C_6Me_6), 3.35 (br s, 2 H, fc), 3.79 (s, 3 H, OMe), 4.10 (d, $^3J_{HH}$ = 5.9 Hz, 2 H, NHC*H*$_2$), 4.41 (br s, 2 H, fc), 4.51 (br s, 2 H, fc), 4.57 (br s, 2 H, fc), 7.28–7.43 (m, 6 H, PPh_2), 7.69–7.92 (br s, 4 H of PPh_2 and 1 H of N*H*CH$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, 50 °C): δ 18.9 (s). IR (KBr): ν_{NH} 3312 m, ν_{CO} 1751 vs, amide I 1651 vs, amide II 1534 vs cm^{-1}. MS (ESI+): *m*/*z* 784 ([M – Cl]$^+$). Anal. Calcd for $C_{38}H_{42}NO_3PCl_2FeRu\cdot0.15CHCl_3$: C, 54.71; H, 5.07; N, 1.67. Found: C, 54.61; H, 4.94; N, 1.61.

Attempted Preparation of [(η^6-*p*-cymene)RuCl$_2$(2-κ*P*)] (5b). The reaction of acid **2** with $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (general procedure) afforded a complicated mixture containing several soluble products (complexes). The composition of the crude reaction mixture changed with reaction time. Repeated attempts to isolate any defined material by column chromatography or crystallization failed.

Preparation of [(η^6-*p*-cymene)RuCl$_2$(3-κ*P*)] (6b). This compound was obtained similarly to complexes **4** from diamide **3** (94 mg, 0.2 mmol) and $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (61 mg, 0.1 mmol). Yield of **6b**: 155 mg (88%), red solid. ^{1}H NMR ($CDCl_3$): δ 0.97 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH*Me*$_2$), 1.78 (s, 3 H, η^6-C_6H_4*Me*), 2.49 (sept, $^3J_{HH}$ = 6.9 Hz, 1 H, *CH*Me$_2$), 3.29 (br s, 2 H, fc), 4.04 (d, $^3J_{HH}$ = 6.1 Hz, 2 H, NHC*H*$_2$), 4.50 (m, 4 H, fc), 4.53 (vt, 2 H, fc), 5.16 (m, 4 H, η^6-C_6H_4), 5.53 (br s, 1 H, CON*H*$_2$), 6.59 (br s, 1 H, CON*H*$_2$), 7.38–7.48 (m, 6 H, PPh_2), 7.72–7.86 (m, 4 H of PPh_2 and 1 H of N*H*CH$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 17.0 (s). IR (KBr): ν_{NH} 3389 s, ν_{NH} 3319 s, amide I 1683 vs, amide I 1647 vs, amide II 1529 s cm^{-1}. MS (ESI+): *m*/*z* 799 ([M + Na]$^+$), 741 ([M – Cl]$^+$). Anal. Calcd for $C_{35}H_{37}N_2O_2PCl_2FeRu\cdot0.85CHCl_3$: C, 49.04; H, 4.35; N, 3.19. Found: C, 49.08; H, 4.28; N, 3.04.

General Procedure for the Preparation of Compounds [(η^6-arene)RuCl(MeCN)(1-κ*P*)][PF$_6$] (7). A solution of **1** (97 mg, 0.2 mmol) in acetonitrile (10 mL) was added to the solid solvento complex $[(\eta^6\text{-arene})Ru(MeCN)_2Cl][PF_6]$ (0.2 mmol). The resulting mixture was stirred at room temperature for 4 h and then evaporated under vacuum. Preparative thin-layer chromatography on silica gel plates with chloroform/acetonitrile (4/1 v/v) afforded the products as yellow solids.

Compound ***7a***. Following the general procedure, $[(\eta^6\text{-}C_6H_6)Ru(MeCN)_2Cl][PF_6]$ (88 mg, 0.2 mmol) and **1** (97 mg, 0.2 mmol) afforded **7a** as a yellow solid. Yield: 99 mg (51%). ^{1}H NMR

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(CD_3CN): δ 2.22 (s, 3 H, MeCN), 3.71 (s, 3 H, OMe), 3.94 (dt, $J \approx$ 1.3, 2.5 Hz, 1 H, fc), 3.96 (d, $^3J_{HH}$ = 6.1 Hz, 1 H, NHCH_2), 3.98 (d, $^3J_{HH}$ = 6.1 Hz, 1 H, NHCH_2), 4.06 (dt, $J \approx$ 1.3, 2.5 Hz, 1 H, fc), 4.14 (m, 1 H, fc), 4.60 (dt, $J \approx$ 1.3, 2.6 Hz, 1 H, fc), 4.66 (m, 2 H, fc), 4.72 (m, 1 H, fc), 4.82 (m, 1 H, fc), 5.64 (s, 6 H, η^6-C_6H_6), 6.99 (t, $^3J_{HH}$ = 6.0 Hz, 1 H, N*H*CH$_2$), 7.51−7.83 (m, 10 H, PPh_2). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (sept, $^1J_{PF}$ = 706 Hz, PF_6), 28.1 (s, PPh_2). $^{19}F\{^1H\}$ NMR (CD_3CN): δ −72.9 (d, $^1J_{PF}$ = 706 Hz, PF_6). IR (KBr): ν_{NH} 3442 m, $\nu_{C\equiv N}$ 2296 w, ν_{CO} 1748 vs, amide I 1651 vs, amide II 1534 vs, ν_{PF} 842 vs cm^{-1}. MS (ESI+): m/z 700 ([M − MeCN − PF_6]$^+$). Anal. Calcd for $C_{34}H_{33}N_2O_3F_6P_2ClFeRu\cdot0.75CHCl_3$: C, 42.79; H, 3.49; N, 2.87. Found: C, 42.84; H, 3.48; N, 2.91.

Compound ***7b***. This compound was prepared similarly from [(η^6-*p*-cymene)Ru(MeCN)$_2$Cl][PF_6] (100 mg, 0.2 mmol) and **1** (97 mg, 0.2 mmol). Yield: 132 mg (65%), yellow solid. ^1H NMR (CD_3CN): δ 0.99 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, CH*Me*$_2$), 1.00 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, CH*Me*$_2$), 1.90 (s, 3 H, η^6-C_6H_4*Me*), 2.15 (s, 3 H, MeCN), 2.35 (sept, $^3J_{HH}$ = 7.0 Hz, 1 H, *CH*Me$_2$), 3.70 (s, 3 H, OMe), 3.85 (dt, $J \approx$ 1.3, 2.5 Hz, 1 H, fc), 3.93 (dt, $J \approx$ 1.3, 2.6 Hz, 1 H, fc), 3.95 (d, $^3J_{HH}$ = 6.1 Hz, 2 H, NHCH_2), 4.00 (m, 1 H, fc), 4.47 (dt, $J \approx$ 1.4, 2.6 Hz, 1 H, fc), 4.61 (dt, $J \approx$ 1.3, 2.6 Hz, 1 H, fc), 4.63 (m, 1 H, fc), 4.73 (m, 2 H, fc), 5.17 (d, J_{HH} = 6.1 Hz, 1 H, η^6-C_6H_4), 5.43 (dt, J_{HH} = 6.2, 1.4 Hz, 1 H, η^6-C_6H_4), 5.50 (d, J_{HH} = 6.5 Hz, 1 H, η^6-C_6H_4), 5.74 (dd, J_{HH} = 6.4, 1.0 Hz, 1 H, η^6-C_6H_4), 6.89 (t, $^3J_{HH}$ = 6.1 Hz, 1 H, N*H*CH$_2$), 7.55−7.94 (m, 10 H, PPh_2). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (sept, $^1J_{PF}$ = 706 Hz, PF_6), 27.7 (s, PPh_2). $^{19}F\{^1H\}$ NMR (CD_3CN): δ −72.9 (d, $^1J_{PF}$ = 706 Hz, PF_6). IR (KBr): ν_{NH} 3418 s, $\nu_{C\equiv N}$ 2293 w, ν_{CO} 1750 s, amide I 1651 s, amide II 1533 s, ν_{PF} 840 vs cm^{-1}. MS (ESI+): m/z 756 ([M − MeCN − PF_6]$^+$). Anal. Calcd for $C_{38}H_{41}N_2O_3F_6P_2ClFeRu\cdot0.55CHCl_3$: C, 45.95; H, 4.16; N, 2.78. Found: C, 55.97; H, 4.11; N, 2.70.

Compound ***7c***. Starting with [(η^6-hexamethylbenzene)Ru(MeCN)$_2$Cl][PF_6] (105 mg, 0.2 mmol) and **1** (97 mg, 0.2 mmol), the general procedure afforded **7c** as a yellow solid. Yield: 150 mg (70%). ^1H NMR (CD_3CN): δ 1.76 (s, 18 H, η^6-C_6Me_6), 2.16 (s, 3 H, MeCN), 3.68 (m, 1 H, fc), 3.70 (s, 3 H, OMe), 3.75 (m, 1 H, fc), 3.96 (br d, $^3J_{HH}$ = 6.1 Hz, 2 H, NHCH_2), 4.28 (br s, 1 H, fc), 4.62 (m, 1 H, fc), 4.50 (m, 2 H, fc), 4.64 (m, 1 H, fc), 4.72 (m, 1 H, fc), 6.92 (t, $^3J_{HH}$ = 5.9 Hz, 1 H, N*H*CH$_2$), 7.50−7.85 (m, 10 H, PPh_2). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (sept, $^1J_{PF}$ = 706 Hz, PF_6), 29.7 (s, PPh_2). $^{19}F\{^1H\}$ NMR (CD_3CN): δ −72.9 (d, $^1J_{PF}$ = 706 Hz, PF_6). IR (KBr): ν_{NH} 3440 m, $\nu_{C\equiv N}$ 2289 w, ν_{CO} 1749 vs, amide I 1653 vs, amide II 1534 vs, ν_{PF} 847 vs cm^{-1}. MS (ESI+): m/z 784 ([M − MeCN − PF_6]$^+$). Anal. Calcd for $C_{40}H_{45}N_2O_3F_6P_2ClFeRu\cdot0.9CHCl_3$: C, 45.59; H, 4.29; N, 2.60. Found: C, 45.48; H, 4.28; N, 2.75.

General Procedure for the Synthesis of Compounds [(η^6-arene)Ru(MeCN)$_2$(1-κP)][PF_6]$_2$ (8). A solution of the respective complex [(η^6-arene)RuCl_2(**1**-κP)] (**4**; 1 equiv) in acetonitrile (2 mL per 0.1 mmol of Ru complex) was treated with the stoichiometric amount of Ag[PF_6] (2 equiv) dissolved in acetonitrile (3 mL per 0.2 mmol of Ag salt). The resulting yellow-orange reaction mixture was stirred at room temperature for 3 h, the precipitated solid (AgCl) was removed by filtration through a PTFE filter, and the filtrate was evaporated under vacuum. The residue was purified by preparative thin-layer chromatography on SiO_2 with $CHCl_3$/acetonitrile (2/1 v/v) as the eluent. When they are analyzed by conventional elemental analysis, the bis(acetonitrile) complexes **8** notoriously give erratic results, very likely due to incomplete combustion.

Compound ***8a***. Starting from **4a** (147 mg, 0.2 mmol) and Ag[PF_6] (101 mg, 0.4 mmol), the general procedure afforded **8a** as a yellow solid. Yield: 92 mg, 44%. ^1H NMR (CD_3CN): δ 2.23 (s, 6 H, MeCN), 3.70 (s, 3 H, OMe), 3.98 (d, $^3J_{HH}$ = 6.1 Hz, 2 H, NHCH_2), 4.21 (vt, 2 H, fc), 4.36 (vq, 2 H, fc), 4.73 (vt, 2 H, fc), 4.90 (vq, 2 H, fc), 5.94 (s, 6 H, η^6-C_6H_6), 6.95 (t, $^3J_{HH}$ = 6.0 Hz, 1 H, N*H*CH$_2$), 7.60−7.77 (m, 10 H, PPh_2). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (sept, $^1J_{PF}$ = 707 Hz, PF_6), 33.7 (s, PPh_2). $^{19}F\{^1H\}$ NMR (CD_3CN): δ −72.8 (d, $^1J_{PF}$ = 706 Hz, PF_6). IR (KBr): ν_{NH} 3417 m, $\nu_{C\equiv N}$ 2330 w and 2302 w, ν_{CO} 1748 s, amide I 1639 s, amide II 1542 s, ν_{PF} 836 vs cm^{-1}. MS (ESI+): m/z 586 ([(C_6H_6)Ru(**1** − H)]$^+$).

Compound ***8b***. This compound was prepared similarly from **4b** (158 mg, 0.2 mmol) and Ag[PF_6] (101 mg, 0.4 mmol) and isolated as a yellow solid. Yield: 122 mg (56%). ^1H NMR (CD_3CN): δ 1.07 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH*Me*$_2$), 1.93 (s, 3 H, η^6-C_6H_4*Me*), 2.29 (s, 6 H, MeCN), 2.49 (sept, $^3J_{HH}$ = 6.9 Hz, 1 H, *CH*Me$_2$), 3.70 (s, 3 H, OMe), 3.97 (d, $^3J_{HH}$ = 6.1 Hz, 2 H, NHCH_2), 4.12 (vt, 2 H, fc), 4.31 (vq, 2 H, fc), 4.67 (vt, 2 H, fc), 4.85 (vq, 2 H, fc), 5.65 (d, $^3J_{HH}$ = 6.5 Hz, 2 H, η^6-C_6H_4), 5.81 (d, $^3J_{HH}$ = 6.5 Hz, 2 H, η^6-C_6H_4), 6.91 (t, $^3J_{HH}$ = 6.0 Hz, 1 H, N*H*CH$_2$), 7.65−7.81 (m, 10 H, PPh_2). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (sept, $^1J_{PF}$ = 707 Hz, PF_6), 33.0 (s, PPh_2). $^{19}F\{^1H\}$ NMR (CD_3CN): δ −72.8 (d, $^1J_{PF}$ = 707 Hz, PF_6). IR (KBr): ν_{NH} 3414 m, $\nu_{C\equiv N}$ 2329 w and 2299 w, ν_{CO} 1747 s, amide I 1638 vs, amide II 1542 s, ν_{PF} 835 vs cm^{-1}. MS (ESI+): m/z 948 ([M − PF_6]$^+$).

Compound ***8c***. Following the general procedure, **4c** (164 mg, 0.2 mmol) and Ag[PF_6] (101 mg, 0.4 mmol) afforded **8c** as a yellow solid. Yield: 123 mg, 55%. ^1H NMR (CD_3CN): δ 1.87 (s, 18 H, η^6-C_6Me_6), 2.35 (s, 6 H, MeCN), 3.70 (s, 3 H, OMe), 3.96 (vt, 2 H, fc), 3.97 (d, $^3J_{HH}$ = 6.1 Hz, 2 H, NHCH_2), 4.41 (vq, 2 H, fc), 4.63 (vt, 2 H, fc), 4.83 (vq, 2 H, fc), 6.90 (t, $^3J_{HH}$ = 6.1 Hz, 1 H, N*H*CH$_2$), 7.63−7.78 (m, 10 H, PPh_2). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (sept, $^1J_{PF}$ = 707 Hz, PF_6), 34.6 (s, PPh_2). $^{19}F\{^1H\}$ NMR (CD_3CN): δ −72.9 (d, $^1J_{PF}$ = 706 Hz, PF_6). IR (KBr): ν_{NH} 3444 m, $\nu_{C\equiv N}$ 2327 w and 2295 w, ν_{CO} 1747 vs, amide I 1639 vs, amide II 1542 vs, ν_{PF} 839 vs cm^{-1}. MS (ESI+): m/z 976 ([M − PF_6]$^+$), 748 ([(C_6Me_6)Ru(**1** − H)]$^+$).

X-ray Crystallography. The diffraction data were collected with a Stoe image plate diffraction system equipped with a ϕ circle goniometer, using Mo Kα graphite-monochromated radiation (λ = 0.710 73 Å; ϕ range 0−200°, 2θ range from 3.0 to 59°, $D_{max} - D_{min}$ = 12.45−0.81 Å). The structures were solved by direct methods using the program SHELXS-97.[32] Refinement and all further calculations were carried out using SHELXL-97.[32] Examination of the structures with PLATON[33] reveals in **4b** additional disordered solvent molecules, while in **8b** voids between anions and cations are observed. Therefore, new data sets corresponding to omission of the missing solvent molecules were generated with the SQUEEZE algorithm[34] and the structures were refined to full convergence. In both structures, the hydrogen atoms were included in their calculated positions and treated as riding atoms using the SHELXL default parameters. The non-hydrogen atoms were refined anisotropically, using weighted full-matrix least squares based on F^2. Crystallographic details are available as Supporting Information (Table S4). The figures were drawn with the PLATON program. The same program was used to perform all geometric calculations.

CCDC-866729 (**4b**·2CH_3OH) and CCDC-866730 (**8b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax, (internat.) +44-1223/336-033; e-mail, deposit@ccdc.cam.ac.uk).

General Procedure for the Oxidation of Secondary Alcohols. The appropriate quantities of the catalyst and alcohol (1 mmol) were mixed with water (4 mL) in an open vial. The oxidizing agent (4 mmol) was added slowly, and the resulting mixture was stirred at room temperature for the given reaction time. Then, it was extracted with diethyl ether (2 × 5 mL) and dried over anhydrous $MgSO_4$. A small aliquot was analyzed by ^1H NMR spectroscopy to determine the conversion. In the case of complete conversion, the extracts were evaporated and the crude product was isolated by flash column chromatography over silica using a hexane/diethyl ether mixture to give pure ketones following evaporation.

Characterization Data of the Oxidation Products. Acetophenone:[35] ^1H NMR ($CDCl_3$) δ 2.61 (s, 3 H, Me), 7.43−7.50 (m, 2 H, C_6H_5), 7.52−7.61 (m, 1 H, C_6H_5), 7.93−7.98 (m, 2 H, C_6H_5). 4′-Fluoroacetophenone:[34] ^1H NMR ($CDCl_3$) δ 2.59 (s, 3 H, Me), 7.09−7.16 (m, 2 H, C_6H_4), 7.96−8.01 (m, 2 H, C_6H_4). 4′-Chloroacetophenone:[34] ^1H NMR ($CDCl_3$) δ 2.59 (s, 3 H, Me), 7.41−7.47 (m, 2 H, C_6H_4), 7.88−7.92 (m, 2 H, C_6H_4). 4′-Bromoacetophenone (ref.[34]): ^1H NMR ($CDCl_3$) δ 2.58 (s, 3 H, Me), 7.58−7.62 (m, 2 H, C_6H_4), 7.79−7.84 (m, 2 H, C_6H_4). 4′-Methylacetophenone:[34] ^1H NMR ($CDCl_3$) δ 2.42 (s, 3 H, *Me*C_6H_4), 2.59 (s, 3 H, Me), 7.23−7.28 (m, 2 H, C_6H_4),

7.83−7.88 (m, 2 H, C_6H_4). 3′-Bromoacetophenone:[36] ^{1}H NMR ($CDCl_3$) δ 2.60 (s, 3 H, Me), 7.35 (t, J_{HH} = 7.9 Hz, 1 H, C_6H_4), 7.69 (dd, J_{HH} = 1.0, 7.9 Hz, 1 H, C_6H_4), 7.88 (d, J_{HH} = 7.8 Hz, 1 H, C_6H_4), 8.09 (br s, 1 H, C_6H_4). 2′-Acetonaphthone:[34] ^{1}H NMR ($CDCl_3$) δ 2.72 (s, 3 H, Me), 7.53 (dt, J_{HH} = 1.1, 6.8 Hz, 1 H, Ar), 7.60 (dt, J_{HH} = 1.2, 6.8 Hz, 1 H, Ar), 7.87 (d, J_{HH} = 6.0 Hz, 1 H, Ar), 7.89 (d, J_{HH} = 8.2 Hz, 1 H, Ar), 7.96 (d, J_{HH} = 8.0 Hz, 1 H, Ar), 8.03 (dd, J_{HH} = 1.7, 8.6 Hz, 1 H, Ar), 8.46 (br s, 1 H, Ar). Benzophenone:[35] ^{1}H NMR ($CDCl_3$) δ 7.46−7.52 (m, 4 H, Ar), 7.57−7.64 (m, 2 H, Ar), 7.78−7.83 (m, 4 H, Ar). 1-Indanone:[37] ^{1}H NMR ($CDCl_3$): δ 2.67−2.72 (m, 2 H, CH_2), 3.12−3.17 (m, 2 H, CH_2), 7.37 (t, J_{HH} = 7.4 Hz, 1 H, Ar), 7.48 (d, J_{HH} = 7.7 Hz, 1 H, Ar), 7.59 (dt, J_{HH} = 1.1, 7.4 Hz, 1 H, Ar), 7.76 (d, J_{HH} = 7.7 Hz, 1H, Ar). 1-Tetralone:[38] ^{1}H NMR ($CDCl_3$) δ 2.10−2.18 (m, 2 H, CH_2), 2.66 (t, J_{HH} = 6.6 Hz, 2 H, CH_2), 2.97 (t, J_{HH} = 6.1 Hz, 2 H, CH_2), 7.25 (d, J_{HH} = 8.2 Hz, 1 H, Ar), 7.31 (t, J_{HH} = 7.5 Hz, 1 H, Ar), 7.47 (dt, J_{HH} = 1.3, 3.7 Hz, 1 H, Ar), 8.04 (dd, J_{HH} = 1.0, 7.8 Hz, 1H, Ar).

■ ASSOCIATED CONTENT

Supporting Information

Text giving alternative syntheses of compounds **7b** and **8b**, tables summarizing complete catalytic results (Tables S1−S3) and relevant crystallographic data (Table S4), and CIF files giving crystal data for **4b**·2CH_3OH and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) NMR spectra recorded shortly after mixing [(η^6-*p*-cymene)$RuCl_2$]$_2$ with **2** in $CDCl_3$ revealed dominant signals due to complex **5b** as the expected bridge-cleavage product and several additional resonances due to unidentified side products (e.g., a P,O chelate or P,O-bridged multinuclear complex). Upon prolonged standing in solution, the amount of the side products increased. Attempts to purify the crude reaction mixture failed.

(11) In the case of **4b**·2CH_3OH, the dihedral angle of planes C(27−32) and [Cl1, Cl2, P1] is 2.0(2)°. The dihedral angle subtended by the C(31−36) and [N2, N3, P1] planes in **8b** is 4.1(3)°.

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■ NOTE ADDED AFTER ASAP PUBLICATION

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