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Neutral and cationic (η^6-arene)-ruthenium(II) complexes containing the iminophosphorane–phosphine ligand $Ph_2PCH_2P(=N$-p-$C_5F_4N)Ph_2$: influence of the arene ring in catalytic transfer hydrogenation of cyclohexanone

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Dedicated to Professor Pascual Royo in recognition of his pioneering work and leadership in the field of Organometallic Chemistry in Spain

Abstract

Ruthenium(II) dimers $[\{Ru(\eta^6\text{-arene})(\mu\text{-}Cl)Cl\}_2]$ (**1a**–**f**) readily react with the iminophosphorane–phosphine ligand $Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2$ (**2**), in dichloromethane at room temperature, to afford the neutral derivatives $[Ru(\eta^6\text{-arene})Cl_2\{k^1\text{-}P\text{-}Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2\}]$ (arene = C_6H_6 (**3a**), 1-^{i}Pr-4-C_6H_4Me (**3b**), 1,3,5-$C_6H_3Me_3$ (**3c**), 1,2,3,4-$C_6H_2Me_4$ (**3d**), 1,2,4,5-$C_6H_2Me_4$ (**3e**), C_6Me_6 (**3f**)). Treatment of **3a**–**f** with $AgSbF_6$ in dichloromethane yields the cationic species $[Ru(\eta^6\text{-arene})Cl\{k^2\text{-}P,N\text{-}Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2\}][SbF_6]$ (**4a**–**f**). The catalytic activity of complexes **3** and **4** in transfer hydrogenation of cyclohexanone by propan-2-ol has been studied. Among them, the cationic derivative $[Ru(\eta^6\text{-}C_6Me_6)Cl\{k^2\text{-}P,N\text{-}Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2\}][SbF_6]$ (**4f**) shows the highest activity. Electrochemical data for **3** and **4** are also reported.

Keywords: Hemilabile ligands; (η^6-Arene)-ruthenium(II) complexes; Catalytic transfer hydrogenation; Iminophosphoranes

1. Introduction

The coordination and organometallic chemistry of heterodifunctional chelating ligands has been extensively studied. Of special interest are those behaving as hemilabile ligands, because they can selectively liberate a coordination site at the metal for substrate binding [1]. The reversible dissociation of one arm of the ligand provides a highly desirable feature in homogeneous catalysis. The chemistry of diphosphine–monoxide ligands $R_2P(CH_2)_nP(=O)R_2$ illustrates successful applications in a large number of catalytic transformations [2]. Although the related heterodifunctional iminophosphorane–phosphine ligands $R_2P(CH_2)_nP(=NR)R_2$, readily accessible via monoimination of diphosphines with azides [3], have shown a great ability for binding to a wide variety of transition metals [3,4], only a few complexes have been used as catalysts. To the best of our knowledge only the catalytic activity of rhodium (methanol carbonylation and hydrogenation of olefins) [4e,4h], and nickel and cobalt compounds (methanol carbonylation) [4e] has been reported to date.

Recently, we described the preparation of the first ruthenium(II) complexes containing hemilabile iminophosphorane–phosphine ligands [5]. They belong to two types of derivatives: (a) neutral k^1-P-monodentate complexes $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2\{k^1\text{-}P\text{-}Ph_2PCH_2P(=NR)Ph_2\}]$ and (b) cationic k^2-P,N-bidentate complexes $[Ru(\eta^6\text{-}p\text{-cymene})Cl\{k^2\text{-}P,N\text{-}Ph_2PCH_2P(=NR)Ph_2\}]^+$. The well-known ability of (η^6-arene)-ruthenium(II) species to act as efficient catalysts in hydrogen transfer

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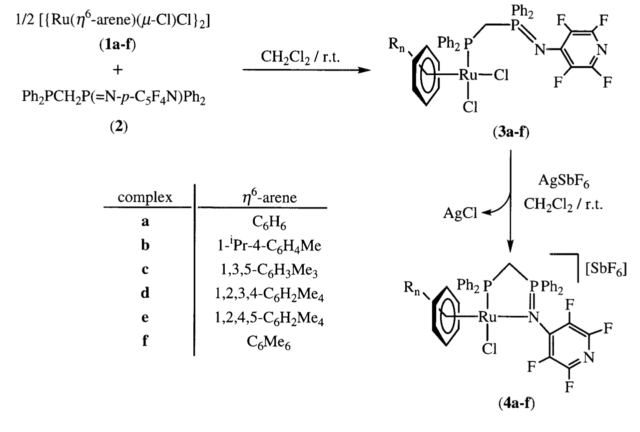
reactions between alcohols and ketones [6] prompted us to study the catalytic activity of the afore-mentioned and analogous derivatives. Thus, in this paper we report: (i) the synthesis and characterization of novel neutral and cationic ruthenium(II) complexes [Ru(η^6-arene)Cl_2(*k*^{1}-*P*-PN)] and [Ru(η^6-arene)Cl(*k*^{2}-*P*,*N*-PN)][SbF_6] (PN=Ph_2PCH_2P(=N-*p*-C_5F_4N)Ph_2) and (ii) the catalytic activity of iminophosphorane–phosphine ruthenium(II) complexes in the transfer hydrogenation of cyclohexanone by propan-2-ol.

2. Results

2.1. Synthesis and characterization of complexes [Ru(η^6-arene)Cl_2{k^1-P-Ph_2PCH_2P(=N-p-C_5F_4N)Ph_2}] and [Ru(η^6-arene)Cl{k^2-P,N-Ph_2PCH_2P(=N-p-C_5F_4N)Ph_2}][SbF_6]

The reaction of the dimers [{Ru(η^6-arene)(μ-Cl)Cl}$_2$] (**1a**–**f**) [7] with two equivalents of the iminophosphorane–phosphine ligand Ph_2PCH_2P(=N-*p*-C_5F_4N)Ph_2 (**2**) [4b], in dichloromethane at room temperature, leads to complexes [Ru(η^6-arene)Cl_2{*k*^{1}-*P*-Ph_2PCH_2P(=N-*p*-C_5F_4N)Ph_2}] (arene = C_6H_6 (**3a**), 1-^{i}Pr-4-C_6H_4Me (**3b**) [5], 1,3,5-$C_6H_3Me_3$ (**3c**), 1,2,3,4-$C_6H_2Me_4$ (**3d**), 1,2,4,5-$C_6H_2Me_4$ (**3e**), C_6Me_6 (**3f**)) in 81–91% yield (see Scheme 1). Treatment of **3a**–**f** with a slight excess of $AgSbF_6$ gives the cationic derivatives [Ru(η^6-arene)Cl{*k*^{2}-*P*,*N*-Ph_2PCH_2P(=N-*p*-C_5F_4N)Ph_2}][SbF_6] (**4a**–**f**) (77–86%, Scheme 1), which are readily formed via N-coordination of the free iminophosphorane group.

Compounds **3a**–**f**, **4a**–**f** have been isolated as air-stable orange solids. They have been characterized by elemental analyses, conductance measurements and NMR (^{1}H-, ^{31}P{^{1}H}-, ^{19}F-, ^{13}C{^{1}H}-) spectroscopy (details are given in Section 4). The room-temperature ^{31}P{^{1}H}-NMR spectra of all these complexes exhibit the expected two doublet signals of an AX spin system in accord with the proposed formulations. Resonance for the neutral complexes **3a**–**f** appear at higher fields (δ 8.30–9.20 (Ph_2P=N) and 22.61–25.40 (Ph_2P); $^2J_{PP}$ = 37.4–39.4 Hz) than those of the corresponding cationic derivatives **4a**–**f** (δ 52.88–55.38 (Ph_2P=N) and 45.92–47.90 (Ph_2P); $^2J_{PP}$ = 14.0–17.7 Hz). ^{19}F-NMR spectra confirm also the mono- or bidentate coordination mode of the iminophosphorane–phosphine ligand **2**. Thus, the spectra of **3a**–**f** display two signals (AA′BB′ spin system; ca. −157 and −98 ppm) which appear at similar chemical shifts to those reported for the free ligand [4b]. In contrast, the spectra of cationic complexes **4a**–**f** show four sets of multiplets indicating the inequivalence of the fluorine nuclei which arises probably from the presence of stereogenic ruthenium atoms. ^{1}H- and ^{13}C{^{1}H}-NMR spectra exhibit signals in accordance with the proposed structures (see Section 4), being the most significant features those concerning the methylenic group of the iminophosphorane–phosphine ligand **2**: (i) (^{1}H-NMR), a doublet of doublets signal for **3a**–**f** (δ 4.25–4.42; $^2J_{HP}$ = $^2J_{HP'}$ = 9.9–10.8 Hz) and one or two unresolved multiplets for **4a**–**f** (δ 3.46–4.18). (ii) (^{13}C{^{1}H}-NMR), a characteristic doublet of doublets resonance in the ranges 22.16–25.82 (**3a**–**f**; J_{CP} = 50.7–57.1 and 16.9–19.2 Hz) and 30.10–33.44 (**4a**–**f**; J_{CP} = 77.4–79.8 and 19.2–20.6 Hz) ppm.



complex	η^6-arene
a	C_6H_6
b	1-^{i}Pr-4-C_6H_4Me
c	1,3,5-$C_6H_3Me_3$
d	1,2,3,4-$C_6H_2Me_4$
e	1,2,4,5-$C_6H_2Me_4$
f	C_6Me_6

Scheme 1. Synthesis of (η^6-arene)-ruthenium(II) complexes containing the iminophosphorane-phosphine ligand Ph_2PCH_2P(= N-*p*-C_5F_4N)Ph_2.

2.2. Electrochemical studies of complexes [Ru(η^6-arene)Cl_2{k^1-P-Ph_2PCH_2P(=N-p-C_5F_4N)Ph_2}] and [Ru(η^6-arene)Cl{k^2-P,N-Ph_2PCH_2P(=N-p-C_5F_4N)Ph_2}][SbF_6]

The redox behavior of complexes **3a**–**f**, **4a**–**f** has been investigated using CV. The CV of all the complexes showed a quasi-reversible oxidation wave corresponding to the Ru^{2+}–Ru^{3+} redox system. Formal potentials ($E^{\circ\prime}$) values (see Table 1) are given versus the [Cp_2Fe]–

Table 1
Electrochemical data for complexes **3a**–**f** and **4a**–**f** [a]

Neutral complexes **3a**–**f**		Cationic complexes **4a**–**f**	
Complex	$E^{\circ\prime}$ (V) [b]	Complex	$E^{\circ\prime}$ (V) [b]
3a	1.09	**4a**	1.06
3b	0.79	**4b**	0.98
3c	0.76	**4c**	0.92
3d	0.65	**4d**	0.56
3e	0.74	**4e**	0.78
3f	0.66	**4f**	0.61

[a] Measured at 0.1 V s^{-1} in dichloromethane with a 0.03 M solution of [^{n}Bu_4N][PF_6] as the supporting electrolyte.

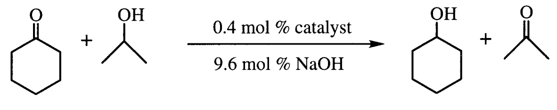
[b] Formal potentials ($E^{\circ\prime}$) are referenced relative to potential of the [Cp_2Fe]–[Cp_2Fe]$^+$ couple (E° = 0.26 V). $E^{\circ\prime}$ = E°(Complex$^+$/Complex) − E°([Cp_2Fe]$^+$/[Cp_2Fe]).

$[Cp_2Fe]^+$ redox couple [8]. For both neutral and cationic complexes, $E^{\circ\prime}$ decreases in the sequence C_6H_6 (**a**) > 1-^{i}Pr-4-C_6H_4Me (**b**) > 1,3,5-$C_6H_3Me_3$ (**c**) > 1,2,4,5-$C_6H_2Me_4$ (**e**) > C_6Me_6 (**f**). Similar trends have been reported for analogous (η^6-arene)-ruthenium(II) complexes [9] in accord with the increasing electron-releasing properties of the arene ring. These observations are also consistent with theoretical studies which indicate that the HOMO energy level decreases when substituting Me by H in an arene-complex [10]. However, $E^{\circ\prime}$ values found for compounds **3d** and **4d**, containing the 1,2,3,4-$C_6H_2Me_4$ ligand, are unexpectedly lower than those of their hexamethylbenzene counterparts **3f** and **4f**, i.e. 0.65 versus 0.66 V and 0.56 versus 0.61 V, respectively. Although we have no explanation for this feature, it is apparent that the hexamethylbenzene derivatives are prone to reduce the electron density of the ruthenium atom in a greater extent than their 1,2,3,4-$C_6H_2Me_4$ counterparts [11].

2.3. Catalytic transfer hydrogenation of cyclohexanone

The catalytic activity of complexes **3a**–**f** and **4a**–**f** in the transfer hydrogenation of cyclohexanone by propan-2-ol has been investigated (Scheme 2). In a typical experiment, the ruthenium(II) catalyst precursor (0.4 mol%) and NaOH (9.6 mol%) were added to a 0.2 M solution of cyclohexanone in ^{i}PrOH at 82 °C, the reaction being monitored by gas chromatography. Selected results are shown in Table 2.

Both neutral **3a**–**e** and cationic **4a**–**e** complexes have proven to be active and efficient catalysts leading to nearly quantitative conversions after 24 h, with no significant difference between the catalytic activity of neutral and the corresponding cationic complex (see entries 1–5 vs. 7–11). However, this does not hold for the complex **3f** with respect to the cationic analogue **4f** (TOF$_{50}$ of 153 vs. 249 h^{-1}; entries 6 and 12) since for the latter a complete conversion of cyclohexanone into cyclohexanol is accomplished after 1 h (entry 12).



Scheme 2. Catalytic transfer hydrogenation of cyclohexanone by propan-2-ol.

Table 2
Transfer hydrogenation of cyclohexanone [a]

Entry	Catalyst	Yield (%) [b]	TOF$_{50}$ (h^{-1}) [c]
[Ru(η^6-arene)Cl_2{k^1-P-Ph_2PCH_2P(=N-p-C_5F_4N)Ph_2}]			
1	**3a**	68 (> 99)	77
2	**3b**	29 (88)	23
3	**3c**	38 (95)	29
4	**3d**	55 (> 99)	59
5	**3e**	43 (98)	37
6	**3f**	73 (> 99)	153
[Ru(η^6-arene)Cl{k^2-P,N-Ph_2PCH_2P(= N-p-C_5F_4N)Ph_2}][SbF_6]			
7	**4a**	71 (> 99)	82
8	**4b**	22 (> 99)	20
9	**4c**	33 (> 99)	28
10	**4d**	53 (> 99)	53
11	**4e**	38 (95)	26
12	**4f**	> 99 [d]	249

[a] Conditions: reactions were carried out at 82 °C using 5 mmol of cyclohexanone (0.2 M in ^{i}PrOH). Ketone/catalyst/NaOH ratio: 250/1/24.

[b] Yield of cyclohexanol after 2.5 h (yield after 24 h in parentheses). GC determined.

[c] Turnover frequencies ((mol product/mol catalyst)/time) were calculated at 50% conversion.

[d] Yield after 1 h.

3. Discussion

Following the synthetic procedure described for the iminophosphorane–phosphine complexes [Ru(η^6-1-^{i}Pr-4-C_6H_4Me)Cl_2{k^1-P-Ph_2PCH_2P(=NR)Ph_2}] and [Ru(η^6-1-^{i}Pr-4-C_6H_4Me)Cl{k^2-P,N-Ph_2PCH_2P(=NR)-Ph_2}][PF_6] [5], a series of analogous derivatives containing η^6-methyl-substituted arene rings, i.e. [Ru(η^6-arene)Cl_2{k^1-P-Ph_2PCH_2P(=N-p-C_5F_4N)Ph_2}] (**3a**, **c**–**f**) and [Ru(η^6-arene)Cl{k^2-P,N-Ph_2PCH_2P(=N-p-C_5F_4-N)Ph_2}][SbF_6] (**4a**, **c**–**f**) (arene = $C_6H_nMe_{6-n}$; $n = 0$, 2, 3, 6), have been prepared in good yields [12]. As expected, in accord with the catalytic activity shown by ruthenium(II) complexes bearing heterodifunctional P,N-ligands [13,14], compounds **3a**–**f** and **4a**–**f** are active in the catalytic transfer hydrogenation of cyclohexanone leading to nearly quantitative formation of cyclohexanol after 24 h. With regard to comparative catalytic performance with respect to analogous complexes, the following features are worth to be noted: (a) in general, the efficiencies are lower than those of neutral octahedral ruthenium(II) complexes bearing bi- or tridentate phosphino-oxazolines, pyridyl-phosphines and imino-phosphines [13]. (b) The catalytic performance shown by the cationic complex **4f** is higher to that recently reported for the related half-sandwich cationic species [Ru(η^6-1-^{i}Pr-4-C_6H_4Me)Cl{k^2-P,N-(N,N-dimethyl-2-diphenylphosphinoethyl)amine}][CF_3SO_3] [14a] and [Ru(η^6-1-^{i}Pr-4-C_6H_4Me)Cl{k^2-P,N-2-(1-N,N-dimethylaminoethyl)-1-diphenylphosphinoferrocene}][CF_3SO_3] [14a], and comparable to that of cationic phosphino–oxazoline complexes [Ru(η^6-C_6H_6)Cl{k^2-P,N-bis(2-oxazolin-2-ylmethyl)phenylphosphine}][CF_3-SO_3] [14b] and [Ru(η^6-1-^{i}Pr-4-C_6H_4Me)Cl{k^2-P,N-(2-oxazolin-2-ylmethyl)diphenylphosphine}][CF_3SO_3] [14c]. In general, the catalytic efficiency seems to be strongly dependent on the arene ligand, the rate order observed being: C_6Me_6 (**f**) > C_6H_6 (**a**) > 1,2,3,4-

$C_6H_2Me_4$ (**d**) > 1,2,4,5-$C_6H_2Me_4$ (**e**) ≈ 1,3,5-$C_6H_3Me_3$ (**c**) > 1-^{i}Pr-4-C_6H_4Me (**b**).

Although no mechanistic studies have been performed, the catalytic transformation most probably follows the classical pathway as is summarized in Scheme 3 [14a]. The active species consists of an *iso*-propoxide complex **A** which, is readily formed from **4** in the presence of a base. Complexes **3** are also suitable precatalysts through an initial chloride dissociation, favored by the polar solvent, which readily leads to complexes **4**. β-elimination from **A** generates the hydride complex **B** [15] to which cyclohexanone coordinates via Ru–N cleavage leading to intermediate **C** [16]. Finally, hydride transfer from ruthenium to the carbonyl group occurs to yield **E** which regenerates **A** by alkoxide exchange.

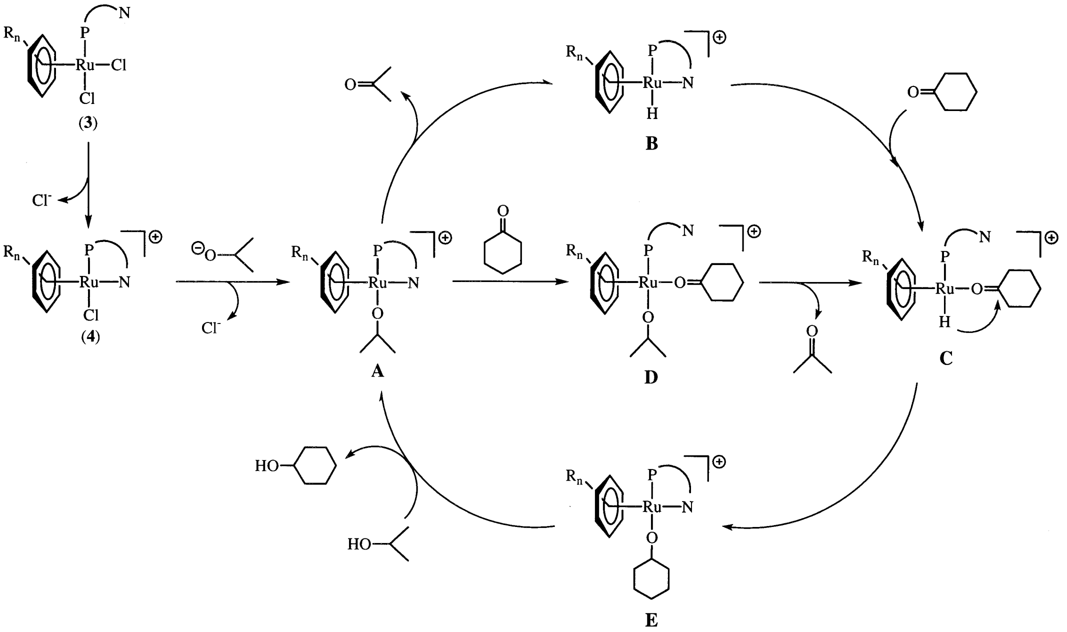
An experimental support of this mechanism relies in the fact that the catalytic activity remains unaffected in the presence of free arene ([arene]/[Ru] = 250/1) or free iminophosphorane–phosphine ligand ([**2**]/[Ru] = 3/1). This clearly indicates that the active species does not result from the dissociation of these ligands in the catalyst precursors **3a**–**f**, **4a**–**f**. Apparently, the catalytic activity of these species does not depend exclusively on the steric or electronic properties of the metal fragment since: (i) the best results have been obtained when benzene and hexamethylbenzene are used (see entries 1, 6, 7 and 12 in Table 2), and (ii) the catalytic rate (see above) does not follow the same trend observed for the oxidation potentials (1,2,3,4-$C_6H_2Me_4$ (**d**) > C_6Me_6 (**f**) > 1,2,4,5-$C_6H_2Me_4$ (**e**) > 1,3,5-$C_6H_3Me_3$ (**c**) > 1-^{i}Pr-4-C_6H_4Me (**b**) > C_6H_6 (**a**)).

4. Experimental

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. Compounds [{Ru(η^6-arene)(μ-Cl)Cl}$_2$] (**1**) [17], $Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2$ (**2**) [4b] and [Ru(η^6-*p*-cymene)Cl_2{κ^1-*P*-$Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2$}] (**3b**) [5] were prepared by following the methods reported in the literature. Gas chromatographic measurements were made on a Hewlett–Packard HP6890 equipment. A HP-INNOWAX cross-linked poly(ethylene glycol) column (30 m, 250 μm) was used. The C, H and N analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Conductivity was measured at room temperature (r.t.), in ca. 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductometer. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), 282.4 MHz (^{19}F) or 75.4 MHz (^{13}C) using $SiMe_4$, C_6F_6 or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported. Abbreviations used: s, singlet; d, doublet; dd, doublet of doublets; m, multiplet.

4.1. Synthesis of [Ru(η^6-arene)Cl_2{k^1-P-$Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2$}] (arene = C_6H_6 (**3a**), 1,3,5-$C_6H_3Me_3$ (**3c**), 1,2,3,4-$C_6H_2Me_4$ (**3d**), 1,2,4,5-$C_6H_2Me_4$ (**3e**), C_6Me_6 (**3f**))

A solution of the iminophosphorane-phosphine ligand $Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2$ (**2**) (1.1 g, 2 mmol) and the corresponding dimer [{Ru(η^6-arene)(μ-Cl)Cl}$_2$]



Scheme 3. Proposed catalytic cycle for the transfer hydrogenation of cyclohexanone by propan-2-ol.

(**1**) (1 mmol) in 50 ml of dichloromethane was stirred at r.t. for 4 h and then evaporated to dryness. The orange solid residue was washed with pentane (3 × 10 ml) and dried in vacuo. Compound **3a**: yield, 1.389 g (87%). Anal. Calc. for $RuC_{36}H_{28}F_4Cl_2N_2P_2$ (798.55 g mol^{-1}): C, 54.15; H, 3.53; N, 3.51. Found: C, 54.01; H, 3.45; N, 3.47%; $^{31}P\{^1H\}$-NMR ($CDCl_3$) $\delta = 9.20$ (d, $^2J_{PP} = 37.4$ Hz, $Ph_2P{=}N$), 22.61 (d, $^2J_{PP} = 37.4$ Hz, Ph_2P) ppm; ^{19}F-NMR ($CDCl_3$) $\delta = -157.13$ and -98.43 (m, 2F each, C_5F_4N) ppm; ^1H-NMR ($CDCl_3$) $\delta = 4.25$ (dd, 2H, $^2J_{HP} = 10.8$ Hz, $^2J_{HP} = 10.8$ Hz, PCH_2P), 5.24 (s, 6H, C_6H_6), 7.19–7.47 (m, 16H, Ph), 7.89–7.95 (m, 4H, Ph) ppm; $^{13}C\{^1H\}$-NMR ($CDCl_3$) $\delta = 22.16$ (dd, $J_{CP} = 57.1$ Hz, $J_{CP} = 19.2$ Hz, PCH_2P), 88.92 (d, $^2J_{CP} = 3.5$ Hz, C_6H_6), 128.20–150.01 (m, Ph and C_5F_4N) ppm. Compound **3c**: yield, 1.530 g (91%). Anal. Calc. for $RuC_{39}H_{34}F_4Cl_2N_2P_2$ (840.63 g mol^{-1}): C, 55.72; H, 4.08; N, 3.33. Found: C, 55.64; H, 4.12; N, 3.19%; $^{31}P\{^1H\}$-NMR ($CDCl_3$) $\delta = 9.12$ (d, $^2J_{PP} = 37.4$ Hz, $Ph_2P{=}N$), 24.02 (d, $^2J_{PP} = 37.4$ Hz, Ph_2P) ppm; ^{19}F-NMR ($CDCl_3$) $\delta = -157.18$ and -98.60 (m, 2F each, C_5F_4N) ppm; ^1H-NMR ($CDCl_3$) $\delta = 1.75$ (s, 9H, CH_3), 4.38 (dd, 2H, $^2J_{HP} = 10.5$ Hz, $^2J_{HP} = 10.5$ Hz, PCH_2P), 4.57 (s, 3H, $C_6H_3Me_3$), 7.13–7.50 (m, 16H, Ph), 7.99–8.06 (m, 4H, Ph) ppm; $^{13}C\{^1H\}$-NMR ($CDCl_3$) $\delta = 18.61$ (s, CH_3), 24.05 (dd, $J_{CP} = 52.4$ Hz, $J_{CP} = 18.6$ Hz, PCH_2P), 86.26 (d, $^2J_{CP} = 4.1$ Hz, CH of $C_6H_3Me_3$), 103.25 (d, $^2J_{CP} = 2.3$ Hz, C of $C_6H_3Me_3$), 127.98–146.09 (m, Ph and C_5F_4N) ppm. Compound **3d**: yield, 1.453 g (85%). Anal. Calc. for $RuC_{40}H_{36}F_4Cl_2N_2P_2$ (854.66 g mol^{-1}): C, 56.21; H, 4.24; N, 3.28. Found: C, 56.02; H, 4.15; N, 3.40%; $^{31}P\{^1H\}$-NMR ($CDCl_3$) $\delta = 8.30$ (d, $^2J_{PP} = 39.4$ Hz, $Ph_2P{=}N$), 25.40 (d, $^2J_{PP} = 39.4$ Hz, Ph_2P) ppm; ^{19}F-NMR ($CDCl_3$) $\delta = -157.15$ and -98.50 (m, 2F each, C_5F_4N) ppm; ^1H-NMR ($CDCl_3$) $\delta = 1.54$ (s, 6H, CH_3), 2.05 (d, 6H, $J_{HH} = 1.9$ Hz, CH_3), 4.13 (d, 2H, $J_{HH} = 1.9$ Hz, $C_6H_2Me_4$), 4.40 (dd, 2H, $^2J_{HP} = 10.2$ Hz, $^2J_{HP} = 10.2$ Hz, PCH_2P), 7.17–7.54 (m, 16H, Ph), 7.85–7.93 (m, 4H, Ph) ppm; $^{13}C\{^1H\}$-NMR ($CDCl_3$) $\delta = 14.04$ and 17.49 (s, CH_3), 23.22 (dd, $J_{CP} = 53.1$ Hz, $J_{CP} = 16.9$ Hz, PCH_2P), 84.12 (s, CH of $C_6H_2Me_4$), 94.92 (s, C of $C_6H_2Me_4$), 105.05 (d, $^2J_{CP} = 11.3$ Hz, C of $C_6H_2Me_4$), 127.86–146.13 (m, Ph and C_5F_4N) ppm. Compound **3e**: yield, 1.504 g (88%). Anal. Calc. for $RuC_{40}H_{36}F_4Cl_2N_2P_2$ (854.66 g mol^{-1}): C, 56.21; H, 4.24; N, 3.28. Found: C, 56.30; H, 4.11; N, 3.20%; $^{31}P\{^1H\}$-NMR ($CDCl_3$) $\delta = 8.98$ (d, $^2J_{PP} = 37.4$ Hz, $Ph_2P{=}N$), 23.02 (d, $^2J_{PP} = 37.4$ Hz, Ph_2P) ppm; ^{19}F-NMR ($CDCl_3$) $\delta = -157.21$ and -98.71 (m, 2F each, C_5F_4N) ppm; ^1H-NMR ($CDCl_3$) $\delta = 1.54$ (s, 12H, CH_3), 4.35 (dd, 2H, $^2J_{HP} = 9.9$ Hz, $^2J_{HP} = 9.9$ Hz, PCH_2P), 4.73 (s, 2H, $C_6H_2Me_4$), 7.18–7.45 (m, 16H, Ph), 7.92 (m, 4H, Ph) ppm; $^{13}C\{^1H\}$-NMR ($CDCl_3$) $\delta = 16.22$ (s, CH_3), 23.68 (dd, $J_{CP} = 54.2$ Hz, $J_{CP} = 18.0$ Hz, PCH_2P), 92.18 (d, $^2J_{CP} = 5.8$ Hz, CH of $C_6H_2Me_4$), 97.50 (s, C of $C_6H_2Me_4$), 127.94–146.10 (m, Ph and C_5F_4N) ppm. Compound **3f**: yield, 1.430 g (81%). Anal. Calc. for $RuC_{42}H_{40}F_4Cl_2N_2P_2$ (882.72 g mol^{-1}): C, 57.15; H, 4.57; N, 3.17. Found: C, 57.11; H, 4.48; N, 3.22%; $^{31}P\{^1H\}$-NMR ($CDCl_3$) $\delta = 9.02$ (d, $^2J_{PP} = 38.1$ Hz, $Ph_2P{=}N$), 24.70 (d, $^2J_{PP} = 38.1$ Hz, Ph_2P) ppm; ^{19}F-NMR ($CDCl_3$) $\delta = -157.33$ and -98.85 (m, 2F each, C_5F_4N) ppm; ^1H-NMR ($CDCl_3$) $\delta = 1.60$ (s, 18H, CH_3), 4.42 (dd, 2H, $^2J_{HP} = 10.2$ Hz, $^2J_{HP} = 10.2$ Hz, PCH_2P), 7.13–7.49 (m, 16H, Ph), 7.97–8.02 (m, 4H, Ph) ppm; $^{13}C\{^1H\}$-NMR ($CDCl_3$) $\delta = 15.34$ (s, CH_3), 25.82 (dd, $J_{CP} = 50.7$ Hz, $J_{CP} = 17.5$ Hz, PCH_2P), 96.74 (d, $^2J_{CP} = 2.9$ Hz, C_6Me_6), 126.93–149.37 (m, Ph and C_5F_4N) ppm.

*4.2. Synthesis of [Ru(η^6-arene)Cl{k^2-P,N-$Ph_2PCH_2P({=}N\text{-}p\text{-}C_5F_4N)Ph_2$}][$SbF_6$] (arene = C_6H_6 (**4a**), 1-^{i}Pr-4-C_6H_4Me (**4b**), 1,3,5-$C_6H_3Me_3$ (**4c**), 1,2,3,4-$C_6H_2Me_4$ (**4d**), 1,2,4,5-$C_6H_2Me_4$ (**4e**), C_6Me_6 (**4f**))*

A suspension of complexes **3a**–**f** (1 mmol) and $AgSbF_6$ (0.378 g, 1.1 mmol) in 40 ml of dichloromethane was stirred in the dark, at r.t., for 4 h. The reaction mixture was then filtered through Kieselguhr and the filtrate concentrated to dryness. The resulting orange solid residue was washed with diethyl ether (3 × 20 ml) and dried in vacuo. Compound **4a**: yield, 0.799 g (80%). Anal. Calc. for $RuC_{36}H_{28}F_{10}N_2P_2ClSb$ (998.84 g mol^{-1}): C, 43.29; H, 2.82; N, 2.80. Found: C, 43.45; H, 2.73; N, 2.78%; conductivity: 110 Ω^{-1} cm^2 mol^{-1}; $^{31}P\{^1H\}$-NMR (CD_2Cl_2) $\delta = 45.92$ (d, $^2J_{PP} = 17.7$ Hz, Ph_2P), 55.38 (d, $^2J_{PP} = 17.7$ Hz, $Ph_2P = N$) ppm; ^{19}F-NMR (CD_2Cl_2) $\delta = -143.30$, -138.13, -89.42 and -89.12 (m, 1F each, C_5F_4N) ppm; ^1H-NMR (CD_2Cl_2) $\delta = 3.65$ and 4.13 (m, 1H each, PCH_2P), 5.51 (s, 6H, C_6H_6), 6.74 (m, 2H, Ph), 7.26–7.77 (m, 18H, Ph) ppm; $^{13}C\{^1H\}$-NMR (CD_2Cl_2) $\delta = 30.10$ (dd, $J_{CP} = 78.6$ Hz, $J_{CP} = 19.8$ Hz, PCH_2P), 89.45 (d, $^2J_{CP} = 1.7$ Hz, C_6H_6), 124.01–147.04 (m, Ph and C_5F_4N) ppm. Compound **4b**: yield, 0.886 g (84%). Anal. Calc. for $RuC_{40}H_{36}F_{10}N_2P_2ClSb$ (1054.95 g mol^{-1}): C, 45.54; H, 3.44; N, 2.65. Found: C, 45.37; H, 3.39; N, 2.50%; conductivity: 107 Ω^{-1} cm^2 mol^{-1}; NMR data in accord with those reported for [Ru(η^6-*p*-cymene)Cl{k^2-*P*,*N*-$Ph_2PCH_2P({=}N\text{-}p\text{-}C_5F_4N)Ph_2$}][$PF_6$] [5]. Compound **4c**: yield, 0.822 g (79%). Anal. Calc. for $RuC_{39}H_{34}F_{10}N_2P_2ClSb$ (1040.92 g mol^{-1}): C, 45.00; H, 3.29; N, 2.69. Found: C, 44.82; H, 3.17; N, 2.77%; conductivity: 114 Ω^{-1} cm^2 mol^{-1}; $^{31}P\{^1H\}$-NMR (CD_2Cl_2) $\delta = 47.10$ (d, $^2J_{PP} = 14.0$ Hz, Ph_2P), 53.58 (d, $^2J_{PP} = 14.0$ Hz, $Ph_2P = N$) ppm; ^{19}F-NMR (CD_2Cl_2) $\delta = -141.43$, -135.97, -90.46 and -89.42 (m, 1F each, C_5F_4N) ppm; ^1H-NMR (CD_2Cl_2) $\delta = 1.85$ (s, 9H, CH_3), 3.86 (m, 2H, PCH_2P), 4.84 (s, 3H, $C_6H_3Me_3$), 6.68 (m, 2H, Ph), 7.21–7.96 (m, 18H, Ph) ppm; $^{13}C\{^1H\}$-NMR (CD_2Cl_2) $\delta = 18.35$ (s, CH_3), 33.15 (dd, $J_{CP} = 79.8$ Hz, $J_{CP} = 19.2$ Hz, PCH_2P), 87.86 (s, CH of $C_6H_3Me_3$), 103.98 (s, C of $C_6H_3Me_3$), 128.67–150.55 (m, Ph and C_5F_4N) ppm. Compound **4d**: yield, 0.907 g (86%). Anal. Calc. for $RuC_{40}H_{36}F_{10}N_2P_2ClSb$ (1054.95 g mol^{-1}): C, 45.54; H, 3.44; N, 2.65. Found: C, 45.42; H, 3.47; N, 2.56%; conductivity: 111 Ω^{-1} cm^2 mol^{-1}; $^{31}P\{^1H\}$-NMR (CD_2Cl_2) $\delta = 46.55$ (d, $^2J_{PP} = 15.7$ Hz, Ph_2P), 52.99 (d, $^2J_{PP} = 15.7$ Hz, $Ph_2P{=}N$) ppm; ^{19}F-NMR (CD_2Cl_2) $\delta = -142.20$, -138.71, -90.11 and -89.80 (m, 1F each, C_5F_4N) ppm; ^1H-NMR (CD_2Cl_2) $\delta = 1.47$, 1.54, 1.84 and 1.88 (s, 3H each, CH_3), 3.60 and 4.18 (m, 1H each, PCH_2P), 4.92 and 5.18 (d, 1H each, $J_{HH} = 5.6$ Hz, $C_6\mathit{H}_2Me_4$), 6.54 (m, 2H, Ph), 7.11–7.95 (m, 18H, Ph) ppm; $^{13}C\{^1H\}$-NMR (CD_2Cl_2) $\delta = 14.39$, 14.50, 17.14 and 18.52 (s, CH_3), 32.67 (dd, $J_{CP} = 78.1$ Hz, $J_{CP} = 19.9$ Hz, PCH_2P), 82.17 (s, CH of $C_6H_2Me_4$), 91.90 (d, $^2J_{CP} = 2.8$ Hz, CH of $C_6H_2Me_4$), 95.78 and 96.26 (s, C of $C_6H_2Me_4$), 104.83 (d, $^2J_{CP} = 5.0$ Hz, C of $C_6H_2Me_4$), 106.38 (d, $^2J_{CP} = 7.8$ Hz, C of $C_6H_2Me_4$), 124.31–147.78 (m, Ph and C_5F_4N) ppm. Compound **4e**: yield, 0.897 g (85%). Anal. Calc. for $RuC_{40}H_{36}F_{10}N_2P_2ClSb$ (1054.95 g mol^{-1}): C, 45.54; H, 3.44; N, 2.65. Found: C, 45.39; H, 3.40; N, 2.71%; conductivity: 105 Ω^{-1} cm^2 mol^{-1}; $^{31}P\{^1H\}$-NMR (CD_2Cl_2) $\delta = 47.90$ (d, $^2J_{PP} = 14.6$ Hz, Ph_2P), 53.67 (d, $^2J_{PP} = 14.6$ Hz, $Ph_2P{=}N$) ppm; ^{19}F-NMR (CD_2Cl_2) $\delta = -142.83$, -136.71, -90.21 and -89.42 (m, 1F each, C_5F_4N) ppm; ^1H-NMR (CD_2Cl_2) $\delta = 1.46$ and 1.86 (s, 6H each, CH_3), 3.96 (m, 2H, PCH_2P), 4.86 (s, 2H, $C_6\mathit{H}_2Me_4$), 6.59 (m, 2H, Ph), 7.21–7.77 (m, 18H, Ph) ppm; $^{13}C\{^1H\}$-NMR (CD_2Cl_2) $\delta = 15.71$ and 16.65 (s, CH_3), 30.33 (dd, $J_{CP} = 78.1$ Hz, $J_{CP} = 20.6$ Hz, PCH_2P), 91.08 (d, $^2J_{CP} = 3.5$ Hz, CH of $C_6H_2Me_4$), 94.65 (s, C of $C_6H_2Me_4$), 104.01 (d, $^2J_{CP} = 5.7$ Hz, C of $C_6H_2Me_4$), 124.83–147.05 (m, Ph and C_5F_4N) ppm. Compound **4f**: yield, 0.834 g (77%). Anal. Calc. for $RuC_{42}H_{40}F_{10}N_2P_2ClSb$ (1083.00 g mol^{-1}): C, 46.58; H, 3.72; N, 2.59. Found: C, 46.31; H, 3.66; N, 2.70%; conductivity: 108 Ω^{-1} cm^2 mol^{-1}; $^{31}P\{^1H\}$-NMR (CD_2Cl_2) $\delta = 47.67$ (d, $^2J_{PP} = 14.6$ Hz, Ph_2P), 52.82 (d, $^2J_{PP} = 14.6$ Hz, $Ph_2P{=}N$) ppm; ^{19}F-NMR (CD_2Cl_2) $\delta = -142.77$, -136.80, -90.12 and -89.31 (m, 1F each, C_5F_4N) ppm; ^1H-NMR (CD_2Cl_2) $\delta = 1.66$ (s, 18H, CH_3), 3.46 and 4.06 (m, 1H each, PCH_2P), 6.22 (m, 2H, Ph), 7.04–7.99 (m, 18H, Ph) ppm; $^{13}C\{^1H\}$-NMR (CD_2Cl_2) $\delta = 15.80$ (s, CH_3), 33.44 (dd, $J_{CP} = 77.4$ Hz, $J_{CP} = 19.7$ Hz, PCH_2P), 98.61 (d, $^2J_{CP} = 2.6$ Hz, C_6Me_6), 126.95–148.50 (m, Ph and C_5F_4N) ppm.

4.3. Synthesis of $[Ru(\eta^6\text{-}1,2,3,4\text{-}C_6H_2Me_4)Cl_2(PR_3)]$ ($PR_3 = PPh_3$ (**5**), PMe_3 (**6**))

A solution of the corresponding phosphine (2 mmol) and the dimer $[\{Ru(\eta^6\text{-}1,2,3,4\text{-}C_6H_2Me_4)(\mu\text{-}Cl)Cl\}_2]$ (**1d**) (0.612 g, 1 mmol) in 50 ml of dichloromethane was stirred at r.t. for 3 h and then evaporated to dryness. The orange solid residue was washed with pentane (3 × 10 ml) and dried in vacuo. Compound **5**: yield, 1.023 g (90%). Anal. Calc. for $RuC_{28}H_{29}Cl_2P$ (568.49 g mol^{-1}): C, 59.16; H, 5.14. Found: C, 58.91; H, 5.20%; $^{31}P\{^1H\}$-NMR ($CDCl_3$) $\delta = 29.30$ (s) ppm; ^1H-NMR ($CDCl_3$) $\delta = 1.84$ and 2.08 (s, 6H each, CH_3), 4.04 (s, 2H, $C_6\mathit{H}_2Me_4$), 7.35 (m, 9H, Ph), 7.77 (m, 6H, Ph) ppm; $^{13}C\{^1H\}$-NMR ($CDCl_3$) $\delta = 13.61$ and 17.36 (s, CH_3), 83.72 (s, CH of $C_6H_2Me_4$), 95.21 (s, C of $C_6H_2Me_4$), 104.71 (d, $^2J_{CP} = 10.5$ Hz, C of $C_6H_2Me_4$), 127.78 (d, $J_{CP} = 9.9$ Hz, CH of Ph), 129.94 (s, CH of Ph), 134.08 (d, $J_{CP} = 9.3$ Hz, CH of Ph), 134.79 (d, $J_{CP} = 45.4$ Hz, C of Ph) ppm. Compound **6**: yield, 0.711 g (93%). Anal. Calc. for $RuC_{13}H_{23}Cl_2P$ (382.28 g mol^{-1}): C, 40.85; H, 6.06. Found: C, 40.71; H, 5.99%; $^{31}P\{^1H\}$-NMR ($CDCl_3$) $\delta = 6.55$ (s) ppm; ^1H-NMR ($CDCl_3$) $\delta = 1.57$ (d, 9H, $^2J_{HP} = 10.2$ Hz, PCH_3), 1.90 (s, 6H, CH_3), 2.10 (d, 6H, $J_{HH} = 2.8$ Hz, CH_3), 4.79 (d, 2H, $J_{HH} = 2.8$ Hz, $C_6\mathit{H}_2Me_4$) ppm; $^{13}C\{^1H\}$-NMR ($CDCl_3$) $\delta = 13.75$ and 18.08 (s, CH_3), 16.96 (d, $J_{CP} = 32.6$ Hz, PCH_3), 79.16 (s, CH of $C_6H_2Me_4$), 93.68 (s, C of $C_6H_2Me_4$), 105.76 (d, $^2J_{CP} = 10.3$ Hz, C of $C_6H_2Me_4$) ppm.

4.4. Electrochemistry

CV measurements (25 °C) were carried out with a three-electrode system. The working electrode was a platinum disk electrode, the counter electrode was a platinum spiral, and the reference electrode was an aqueous saturated calomel electrode (SCE) separated from the solution by a porous septum. Current and voltage parameters were controlled using a PAR system M273. In a typical experiment, 0.15 mmol of the complex was dissolved under a nitrogen atmosphere in 10 ml of freshly distilled and deoxygenated dichloromethane containing 1.15 g of pure $[^nBu_4N][PF_6]$ (0.3 mmol) as electrolyte. Formal CV potentials ($E^{\circ\prime}$) are referenced relative to potential of the $[Cp_2Fe]$–$[Cp_2Fe]^+$ couple ($E^\circ = 0.26$ V) run under identical conditions ($E^{\circ\prime} = E^\circ(\text{Complex}^+/\text{Complex}) - E^\circ([Cp_2Fe]^+/[Cp_2Fe])$) [8].

4.5. General procedure for catalytic transfer hydrogenation of cyclohexanone

Under inert atmosphere cyclohexanone (0.49 g, 5 mmol), the ruthenium catalyst precursor (0.02 mmol, 0.4 mol%), and 20 ml of propan-2-ol are introduced in a Schlenk tube fitted with a condenser and heated at 82 °C for 15 min. Then NaOH is added (5 ml of a 0.096 M solution in propan-2-ol, 9.6 mol%) and the reaction is monitored by gas chomatography. Cyclohexanol and acetone are the only products detected in all cases.

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[15] Attempts to synthesize hydride derivatives **B** by reaction of complexes **4** with one equivalent of NaOH in propan-2-ol failed obtaining instead complicated mixtures of uncharacterized species.

[16] Alternatively, transformation of **A** into **C** could involve intermediate **D** formed by coordination of cyclohexanone to **A** via chelate ring openning. In fact, $^{31}P\{^1H\}$-NMR spectra of the catalytic reaction mixtures showed, after 15 min, resonances typical of two AB systems at ca. 28 and 4 ppm ($^2J_{PP} = 24$ Hz), and 21 and 1 ppm ($^2J_{PP} = 27$ Hz), which are consistent with a monodentate coordination of the ligand **2** [5].

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