Synthesis of Imidazolium-Tethered Ruthenium(II)-Arene Complexes and Their Application in Biphasic Catalysis

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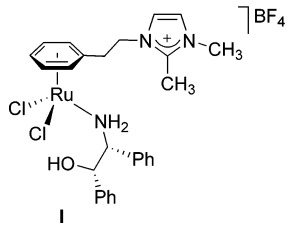
Reaction of $RuCl_3$ with 1-[2-(1,4-cyclohexadiene-1-yl)alkyl]-3-methylimidazolium chloride (alkyl = ethyl, butyl) and 1-[2-(1,4-cyclohexadiene-1-yl)ethyl]-2,3-dimethylimidazolium chloride affords a series of dimeric ruthenium complexes of the type $[RuCl_2(\eta^6\text{-arene})]_2Cl_2$. Treatment of these dimeric salts with phosphine ligands leads to the highly water-soluble monomeric complexes $[RuCl_2PR_3(\eta^6\text{-arene})]Cl$ (PR_3 = PPh_3, PCy_3). Reaction of $[RuCl_2(\eta^6\text{-1-(2-benzylethyl)-3-butylimidazolium})]Cl$ with Ag_2O gives rise to a η^6-arene-carbene chelate complex. The phosphine complexes have been tested as catalysts in the hydrogenation of styrene immobilized in water or an ionic liquid and in the aqueous reduction of CO_2/CO_3^{2-}. A carbonate-hydride complex has been identified as intermediate by high-pressure NMR measurements. The solid-state structures of several of the new imidazolium-functionalized arene complexes including the arene-carbene chelate complex are reported.

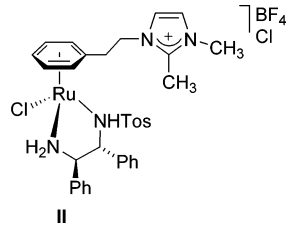
1. Introduction

The first examples of biphasic catalysis date back several decades to the pioneering work of Parshall,[1] Joó,[2] and Manassen.[3] The concept has since been employed in large-scale industrial processes such as the Shell Higher Olefin Process[4] and the Rhône-Poulenc-Ruhrchemie hydroformylation process,[5] which has generated considerable interest in the field, and water, perfluorinated solvents, ionic liquids, and supercritical fluids have all been extensively used to immobilize catalysts.[6]

Numerous well-characterized catalysts have been tested in biphasic ionic liquid processes, often affording good results, with the catalyst frequently displaying increased stability and activity in these media.[7] However, neutral catalysts are often only poorly retained in water and ionic liquids and are lost during product isolation. Accordingly, some effort has been devoted to both the design of catalysts that specifically operate in polar (ionic) media and the design of ionic liquids that enhance catalyst retention.[8] One of the most effective ways to prevent catalyst leaching into the organic (product) phase is by employing complexes bearing ligands with charged moieties. In particular, phosphine ligands with a variety of charged groups including sulfonate, imidazolium, guanidinium, and pyridinium, to name a few, have been prepared and shown to facilitate catalyst retention in water and ionic liquids.[7,9] However, modification of a given phosphine ligand is not always straightforward, and attaching charged groups to other types of ligands may be advantageous. In this context, we recently described the synthesis of the imidazolium-tagged ruthenium(II)-arene complexes **I** and **II** and demonstrated their utility as transfer-hydrogenation catalysts.[10]



I



II

The main advantage of functionalizing the η^6-arene with a charged moiety lies in the fact that no modification of the chiral amine ligands is required and that other, readily available ligands could be easily screened with respect to their performance under biphasic conditions. We now wish to disclose further reactivity studies of ruthenium complexes with imidazolium moieties tethered to the complexed arene, together with X-ray diffraction data, and we describe the application of some of the newly obtained compounds in the biphasic reduction of styrene and CO_2.

2. Results and Discussion

Ruthenium complexes of the type $[RuCl_2(\eta^6\text{-arene})]_2$ are generally prepared via reaction of cyclohexadienes with ruthenium(III) chloride in alcoholic media, although subsequent arene-exchange reactions expand the range of arenes that can be complexed.[11] The route used to prepare the complexes

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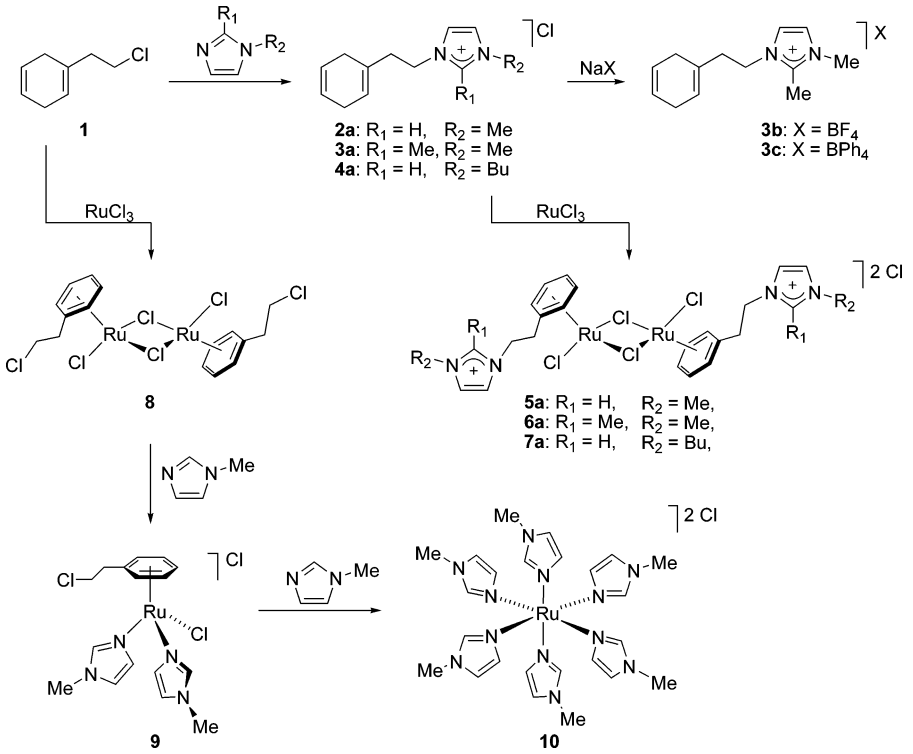
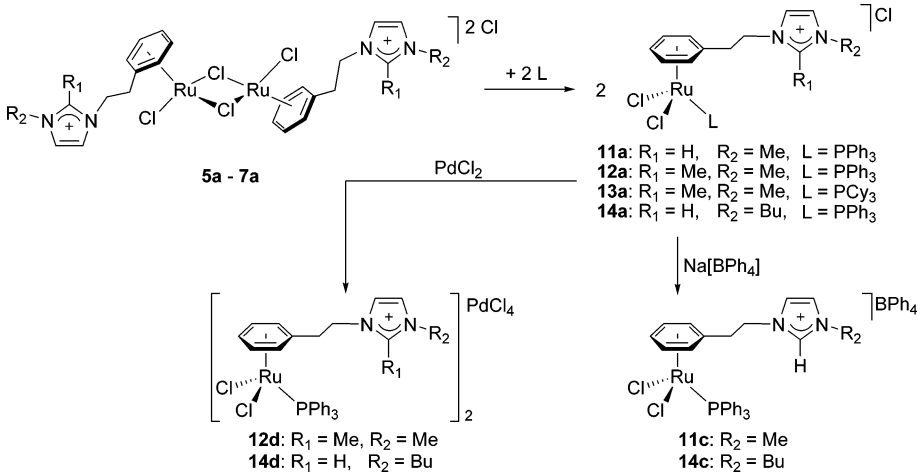
Scheme 1



Scheme 2



described herein, bearing η^6-arenes with pendant imidazolium tags, is depicted in Scheme 1. Birch reduction of 1-phenyl-2-ethanol and subsequent chlorination affords 1-(2-chloroethyl)-1,4-cyclohexadiene, **1**, which reacts with alkylimidazoles to give the imidazolium chlorides **2a**−**4a** in good yield. Exchange of the chloride counterion for other anions such as $[BF_4]^-$ and $[BPh_4]^-$ may be desirable either to alter the solubility of these imidazolium salts or to decrease the melting point with the preparation of new ionic liquids in mind.[12] To obtain crystals for X-ray diffraction studies (see below), the chloride anion in **3a** was exchanged for tetraphenylborate, affording **3c**.

Reduction of ruthenium(III) chloride in methanol in the presence of an excess of **2a**−**4a** leads to the dimeric complexes **5a**−**7a** in excellent yield. An alternative pathway, involving initial complexation of **1** to ruthenium to afford the dimeric complex **8** prior to the reaction with an alkylimidazole, did not lead to the envisaged quaternization of the imidazole nitrogen, but to the bis-imidazole complex **9** in near-quantitative yield. In the presence of an excess of imidazole, the η^6-arene moiety is lost, and a dicationic homoleptic imidazole complex, **10**, is formed.

The dimeric, dicationic complexes **5a**−**7a** are highly soluble in donor solvents such as water, DMSO, and DMF, but essentially insoluble in alcohols and chlorinated solvents. Reaction with simple phosphines, e.g., PPh_3 and PCy_3, leads to the monomeric phosphine complexes **11**−**14**, as shown in Scheme 2, which are all highly water-soluble, but also dissolve in, for example, CH_2Cl_2. All complexes were fully characterized by mass spectrometry, NMR spectroscopy, and elemental analysis, with selected NMR data provided in Table 1 (see X-ray

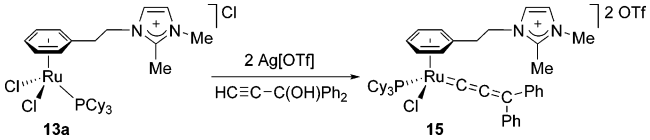
(12) The BF_4 salt **3b** has a melting point of 85 °C and could accordingly be classed as an ionic liquid. However, at this temperature, the viscosity is very high and preparation of the Tf_2N analogue is probably required to obtain a true low-melting ionic liquid.

Table 1. Selected ^{13}C and $^{31}P\{^1H\}$ NMR Spectroscopic Data

	C1	C2/6	C3/5	C4	C9	P
5a[a]	101.6	87.0	88.8	85.1	137.5	
6a[a]	101.3	87.3	88.5	85.3	145.1	
7a[a]	101.7	86.8	88.8	85.0	136.7	
8[a]	102.6	87.2	88.5	85.0	136.7	
9[b]	99.8	83.8	87.4	82.4	142.2	
11a[b]	107.7	89.6	87.5	82.4	139.2	29.4
12a[b]	106.6	90.4	86.8	82.5	144.3	28.7
13a[b]	106.3	90.7	83.0	78.1	144.3	31.8
14a[b]	107.9	89.4	87.5	82.4	137.9	29.5
16[c]	91.1	78.5	94.7	90.8	167.8	

[a] In d_6-DMSO. [b] In $CDCl_3$. [c] In CD_2Cl_2.

Scheme 3



structures for the numbering scheme).

To obtain crystals suitable for X-ray diffraction analysis, anion metathesis with $Na[BPh_4]$ was undertaken, affording salts **11c** and **14c**, while reaction with $PdCl_2$ gives **12d** and **14d**, respectively. The PCy_3 adduct **13a** was initially prepared with the aim of generating an allylidiene complex via reaction with 1,1-diphenyl-2-propyn-1-ol, as outlined in Scheme 3. The η^6-*p*-cymene analogue of **15** has been previously demonstrated to be an active catalyst for the ring-closing metathesis of olefins.[13] After anion metathesis and chloride abstraction with 2 equiv of silver triflate, 1,1-diphenylpropynol was added, affording a purple solution. In situ ^{31}P NMR measurements suggest the formation of **15** from the presence of a resonance at ca. 60 ppm; however rapid decomposition was observed and isolation of **15** has not, as yet, been achieved. The reason for the apparent instability of the allylidene compound may be 2-fold. First, the monosubstituted arene (relative to for example *p*-cymene or hexamethylbenzene, which both provide the desired allylidene complexes) may not provide sufficient steric protection. Second, the presence of an additional charge and correspondingly a higher anion concentration may lead to increased decomposition via nucleophilic attack.

Imidazolium salts represent excellent precursors to carbene ligands, generated either deliberately[14] or formed in situ during CC-coupling reactions with simple palladium salts as precatalysts in imidazolium-based ionic liquids.[15] Following the procedure recently described by Jóo et al.,[16] complex **7a** was treated with silveroxide, which acts a both base and chloride scavenger, affording the carbene complex **16**, as shown in Scheme 4.

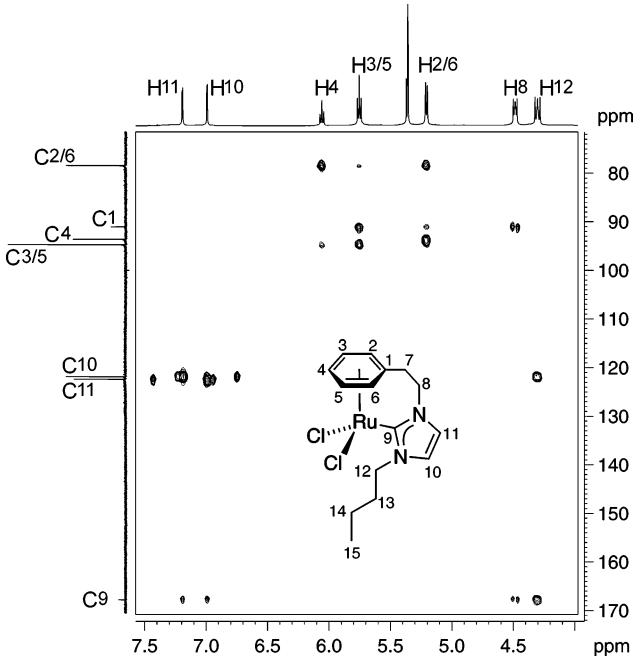
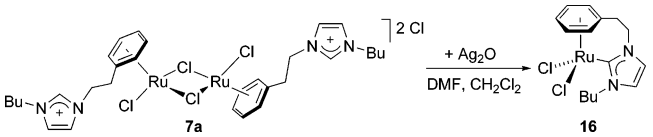


Figure 1. CH long-range correlation spectrum of **16** showing the diagnostic cross-peaks to the carbene carbon C9 arising from $^3J_{CH}$ coupling interactions stemming from H8, H10, H11, and H12.

Scheme 4



Several ruthenium carbene complexes have been prepared from ruthenium dimers of the type $[RuCl_2(arene)]_2$ in a similar manner, with either Cs_2CO_3[17] or Ag_2O[16] as base. Complexes closely related to **16** also containing an arene-imidazolylidene ligand have been previously reported by Dixneuf and coworkers.[18] However, in their route the carbene complex was generated prior to coordination of the tethered arene moiety, which was accomplished in a second step by thermal exchange of η^6-*p*-cymene, and other examples leading to comparable chelating arene-carbene complexes are also known.[19] The synthesis of **16** was less straightforward than anticipated, due to solubility problems. Accordingly, **7a** was first dissolved in DMF (presumably forming a monomeric DMF adduct) prior to the reaction with Ag_2O in dichloromethane. In this manner, synthesis of the envisaged carbene complex was possible, though in only moderate yield. Complex **16** was readily identified by ^{13}C NMR spectroscopy from the shift of C9 to markedly higher frequency, viz., 167.8 ppm. The CH long-range correlation spectrum of **16** is depicted in Figure 1, showing the diagnostic cross-peaks to the carbene carbon C9 stemming from hydrogen atoms *meta* to C9, namely, atoms H8, H10, H11, and H12. Relative to the starting material, complexation of the carbene leads to a shift to lower frequency of ca. 10 ppm of C1 and C2/6, whereas C3/5 and C4 are shifted to higher frequency. This observation is probably a reflection of the arene plane being somewhat tilted, leading to variations in the strength of the metal−carbon bonds.

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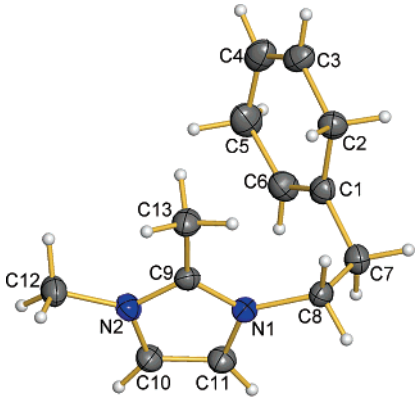

Figure 2. ORTEP plot of the cation of **3c**. Ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): C1−C2 1.502(4), C2−C3 1.490(5), C3−C4 1.319(5), C4−C5 1.493(5), C5−C6 1.492(5), C1−C6 1.333(4), N1−C9 1.334(4), N2−C9 1.342(4), N1−C11 1.382(4), N2−C10 1.389(4), C10−C11 1.343(4), N1−C9−N2 107.7(2).

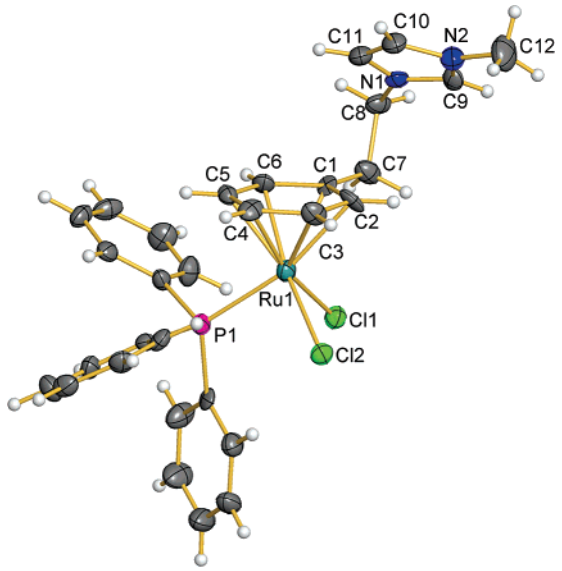

Figure 3. ORTEP plot of the cation of **11c**. Solvent H_2O has been omitted for clarity; ellipsoids are drawn at the 50% probability level.

Solid-State Characterization of 3c, 11c, 12d, 14c, and 16. Crystals of **3c** were obtained from slow diffusion of diethyl ether into CH_2Cl_2, and the structure is shown in Figure 2, with principle bond lengths and angles provided in the caption. Bonding parameters are as expected, with localized C═C double bonds between C1−C6 and C3−C4 being 1.333(4) and 1.319(5) Å, respectively, confirming the presence of the anticipated 1,4-diene from the Birch reduction.

Crystals of the triphenylphosphine derivatives **11c** and **14c** were grown from slow diffusion of diethyl ether into dichloromethane solutions; those of **12d**, from diffusion of diethyl ether into a acetonitrile solution. Their structures are shown in Figures 3−5. Complexation of the arene does not affect the bonding within the imidazolium moiety, and bond distances and angles are essentially identical within experimental errors in all structures. A selection of key bond distances and angles is provided in Table 2 for comparison purposes, and these parameters are in good agreement with other structures of the type $RuCl_2(\eta^6\text{-arene})PR_3$.[20] Crystal packing and weak hydrogen-bonding interactions are probably responsible for the different orientations of the imidazolium ring relative to the plane of the coordinated arene, with dihedral angles between the planes of the two rings being 36.2(2)°, 15.4(6)° and 49.4(1)° for **11c**, **12d**, and **14c**, respectively.

The structure of the carbene complex **16** is depicted in Figure 6. The coordinated arene is slightly tilted, with four shorter ruthenium−carbon bonds to C1, C2, C3, and C6 [2.172(4)−2.178(4) Å] and two longer bonds to C4 and C5 [2.267(5) and 2.280(4) Å]. Coordination of the imidazolinylidene moiety to the metal leads to a moderate lengthening of C9−N1 and C9−N2, 1.386(5) Å, relative to the free imidazolium [cf. 1.33−1.34 Å] and also longer than in a related imidazolinylidene carbene complex.[17] Nevertheless, these bonds are still markedly shorter than those typical of nitrogen−carbon single bonds. Formation of the new metal−carbene bond [Ru−C9 2.089(4) Å] leads to an elongation of the Ru−Cl distances [2.437(1) and 2.459(1) Å] relative to the phosphine complexes. The dihedral angle between the plane of the arene and the plane of the imidazolinylidene is 44.1(1)°, being affected by an intramolecular hydrogen bond, Cl2···H12B 2.46 Å, which appears to hold the butyl chain in place.

Hydrogenation Reactions. The utilization of the imidazolium-tagged Ru-arene complexes **I** and **II** (see Introduction) in ionic liquid biphasic asymmetric transfer-hydrogenation of aryl ketones has been reported previously,[10] and it was demonstrated that the presence of a charged moiety on the complexed arene reduces leaching of the catalyst markedly without having a detrimental effect on the enantioselectivity. Due to their excellent water solubility, complexes **12a**, **14a**, and **16** were tested as catalysts in the biphasic aqueous hydrogenation of styrene to ethylbenzene. For reasons of comparison, **14a** was also evaluated in the ionic liquid *N*-ethyl-3-methylpiccolinium bistrifluormethanesulfonimide, [C_2pic][OTf], and the results are summarized in Table 3. In water, the complexes showed moderate activity, while compound **14a**, when immobilized in [C_2pic][OTf], afforded markedly lower reaction rates. Recently, it has been shown that chloride solvation may be thermodynamically unfavorable in ionic liquids,[21] and the presence of water may therefore be required to generate a catalytically active species should dissociation of a chloride ligand be a step in the catalytic cycle, which is likely to be the case here.[22] Immobilization of the catalysts in water results in slight leaching of the catalyst into the organic phase, whereas in the ionic liquid−organic system no catalyst loss was observed. Accordingly, recycling of **12a** and **14a** was possible, albeit with a moderate decrease in activity. In the course of the catalytic runs the color of the aqueous solution changed from orange to brown-purple, whereas the ionic liquid solution remained orange, and on the basis of ^{31}P NMR spectroscopy it appears that the complex remains unchanged in the ionic liquid (only one peak is observed at δ = 28.2 pm). After reaction, the aqueous catalyst phase was examined using ESI-MS and NMR spectroscopy. The aqueous solution containing **12a** did not show any prominent peaks, nor did the ^{31}P NMR spectrum, and the fate of the precatalyst could not be discerned. In contrast, aqueous solutions of **14a** after catalysis displayed a strong peak at m/z = 593 in the ESI-MS, corresponding to a species that, on the basis of the isotope pattern, no longer contains any chloride ligands, viz., [$Ru(H)_2$-

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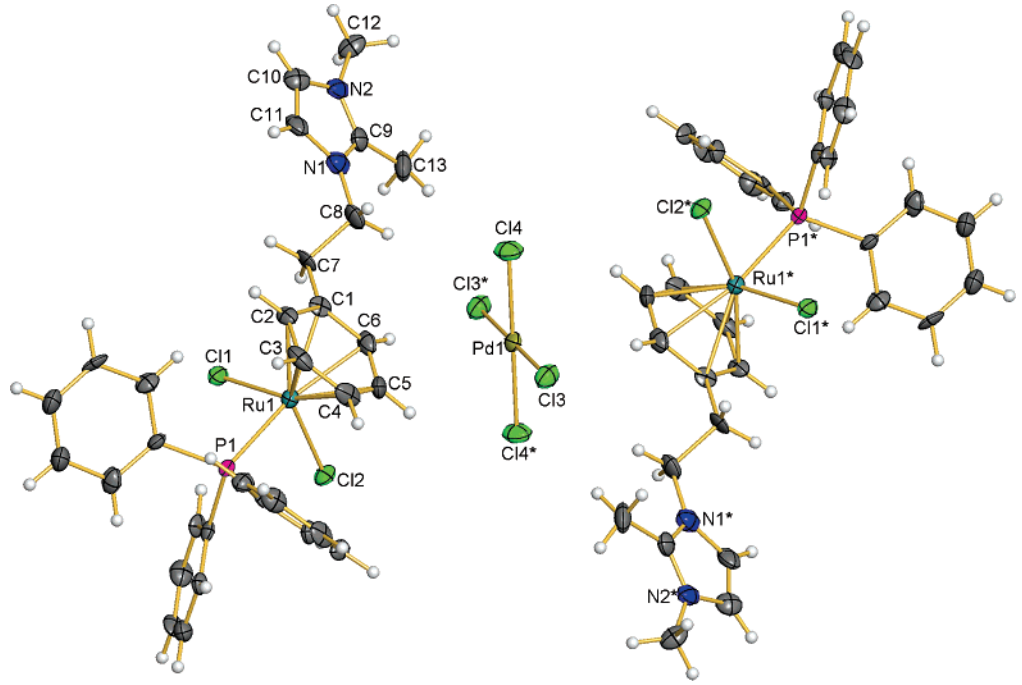


Figure 4. ORTEP plot of **12d**. Ellipsoids are drawn at the 50% probability level. The starred atoms are obtained by the symmetry operation $1-x$, $1-y$, $1-z$.

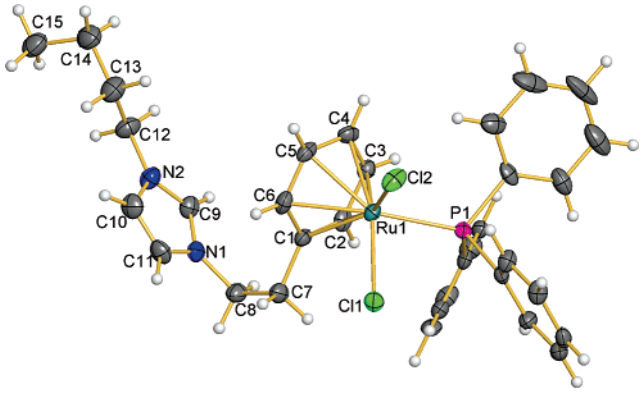


Figure 5. ORTEP plot of the cation of **14c**. Ellipsoids are drawn at the 50% probability level.

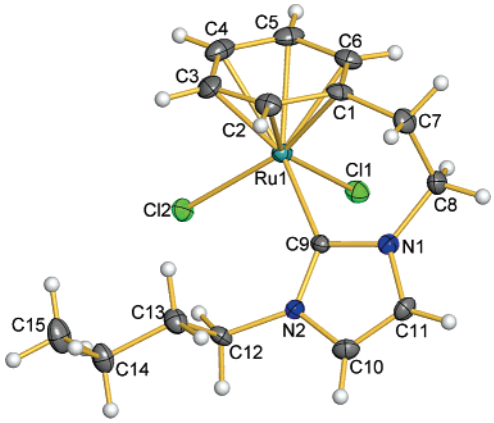


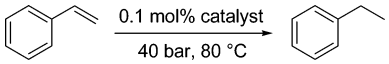
Figure 6. ORTEP plot of **16**. Ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 11c, 12d, 14c, and 16

	11c	12d	14c	16
Ru−Cl1	2.403(2)	2.424(3)	2.4192(10)	2.4374(10)
Ru−Cl2	2.423(2)	2.409(2)	2.4094(10)	2.4593(11)
Ru−P1	2.364(2)	2.373(3)	2.3600(10)	
Ru−C1	2.210(7)	2.288(9)	2.197(4)	2.178(4)
Ru−C2	2.230(7)	2.207(9)	2.211(4)	2.172(4)
Ru−C3	2.209(8)	2.199(10)	2.183(4)	2.172(4)
Ru−C4	2.224(9)	2.195(10)	2.224(4)	2.267(5)
Ru−C5	2.162(8)	2.174(9)	2.238(4)	2.280(4)
Ru−C6	2.181(7)	2.260(9)	2.238(4)	2.174(4)
Ru−C9				2.089(4)
Cl1−Ru−Cl2	86.82(7)	90.95(9)	88.11(4)	87.21(4)
Cl1−Ru−P1	84.44(8)	87.84(9)	82.91(4)	
Cl2−Ru−P1	92.70(7)	84.56(8)	91.25(4)	
Cl1−Ru−C9				84.58(11)
Cl2−Ru−C9				96.66(10)

$(\eta^6$-arene)$(PPh_3)]^+$. In situ ^{31}P NMR measurements of the aqueous solution of **14a** after two catalytic runs revealed a main signal at ca. 55 ppm, which is close in value to the previously reported ruthenium-phosphine-carbene-hydride complex RuH-$(\eta^6$-$C_6H_5OH)(PPh_3)$(carbene).[23] To probe the nature of the species further, the solution was evaporated to dryness and the residue redissolved in $CDCl_3$. The $^{31}P\{^1H\}$ NMR of this solution showed one main peak at 54.8 ppm, together with a signal of low relative intensity at 33.8 ppm, and the ^1H NMR spectrum revealed the presence of hydrides, i.e., a doublet at −8.41 ppm, $J_{PH} = 44$ Hz, and a broad signal at −17.82 ppm. It is tempting to assume that the differences between **12a** and **14a** are a

Table 3. Styrene Hydrogenation[a]



	Run 1 [%]	Run 2 [%]	Run 3 [%]
	run 1 [%]	run 2 [%]	run 3 [%]
12a-H_2O	>99	97	97
14a-H_2O	98	85	75
14a-IL	11	10.5	14
16-H_2O	22	26.5	29.5

[a] S/C ratio = 1000, $p = 40$ bar, $T = 80$ °C, $t = 120$ min; average from 3 experiments.

(23) Abdur-Rashid, K.; Fedorkiw, T.; Lough, A. J.; Morris, R. H. *Organometallics* **2004**, *23*, 86.

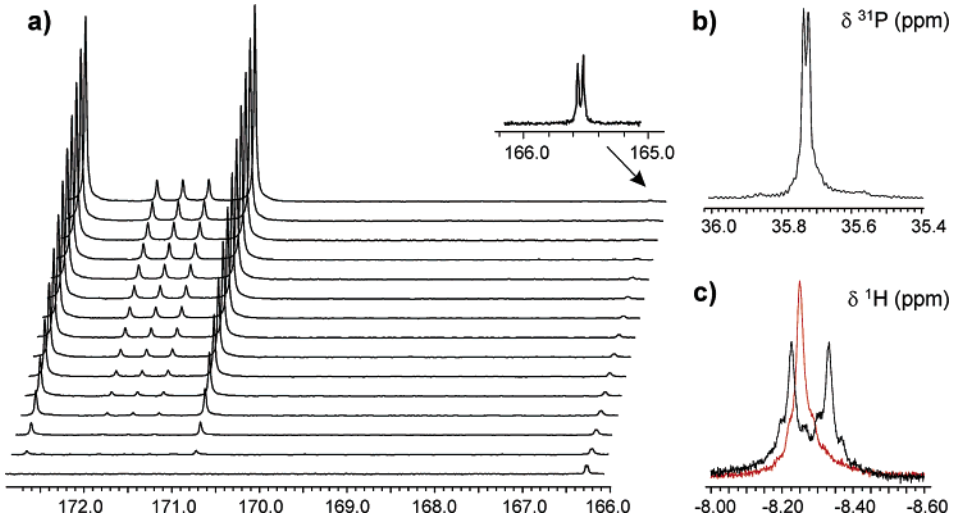


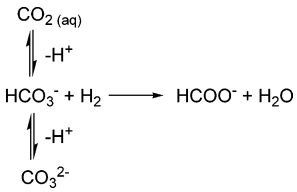
Figure 7. (a) Evolution of the ^{13}C NMR signals stemming from formate $[H^{13}COO]^-$ (δ = 171.7 ppm, $^1J_{CH}$ = 194), deuterated formate $[DC^{13}OO]^-$ (δ = 171.6 ppm, $^1J_{CD}$ = 30), and an intermediate bicarbonate complex **17** (δ = 166.0 ppm, $^3J_{PC}$ = 2.4), with time followed in situ at 333 K. The time delay between each spectrum is 1 h. Initial conditions: $[NaH^{13}CO_3]$ = 0.10 M, [**12a**] = 0.0011 M, $p(CO_2)$ = 0 bar, $p(H_2)$ = 100 bar. (b) $^{31}P\{^1H\}$ NMR spectrum of **17** (δ = 35.7 ppm, $^3J_{CP}$ = 2.4). (c) ^1H NMR spectrum of the hydride region of **17** (δ = −8.25 ppm, $^2J_{PH}$ = 42; red: P-decoupled).

consequence of the presence of an acidic proton at C9 in **14a**, which could interact with the ruthenium center, ultimately affording a carbene complex. However, no direct evidence for the formation of a carbene species was found, i.e., any signal in the ^{13}C NMR at ca. 160 ppm. With **16** as catalyst precursor, a modest increase of activity is observed with each batch, and this is indicative for the increased formation of catalytically active nanoparticles during recycling.[24]

The catalytic hydrogenation of carbon dioxide into useful products is a major challenge, and with the huge amount of limestone available and large quantities of carbon dioxide being emitted as waste from the combustion of fossil raw materials, it could become an important C1-unit in synthetic chemistry. Significant results have been achieved in the hydrogenation of CO_2 into formic acid derivatives in the presence of amines using Rh(I)- and Ru(II)-phosphine catalysts in organic solvents,[25] aqueous solutions,[26] and supercritical CO_2.[27] Recently, it has been found that Ru(II)-arene complexes can been used as catalysts or catalyst precursors in the hydrogenation of CO_2 in aqueous solution if hydrophilic phosphine ligands are present.[28] Accordingly, complexes **11a**, **12a**, and **13a** were tested as potential catalysts for the hydrogenation of CO_2, bicarbonate, and carbonate (see Scheme 5).

Reactions were followed by in situ ^{13}C NMR spectroscopy at 333 K under 100 bar H_2 pressure using a mixture of H_2O/D_2O as solvent, and formate was detected as the only product. Initially only the signal of $[HCOO]^-$ was observed (δ = 171.7 ppm, $^1J_{CH}$ = 194 Hz) with the appearance of the ^{13}C resonance of $[DCOO]^-$ (δ = 171.6 ppm, $^1J_{CD}$ = 30 Hz), as shown in Figure 7, occurring with time.

Scheme 5



A fast catalytic deuterium exchange between H_2/D_2O and the formate is not unexpected since ruthenium-phosphine complexes are known to catalyze H−D exchange in water.[29] Kinetic data was obtained using the sum of the integrals stemming from the $[HCOO]^-$ and $[DCOO]^-$ resonances relative to the integral of the $[HCO_3]^-$ resonance (plots are shown in the Supporting Information). No induction period was observed, and the initial reaction rates were determined from the slope of the curves at time zero, expressed as catalyst turnover frequencies (TOF). At T = 333 K and $p(H_2)$ = 100 bar, the TOFs of **11a**, **12a**, and **13a** are 5, 9, and 4 mol·mol^{-1}·h^{-1}, respectively, and conversion at the end of the reaction varied between 61 and 84%, depending on the reaction conditions.

While the activity in aqueous catalytic hydrogenation reactions often depends on the pH of the solution,[30] no significant effect on the reaction rate was observed with complexes **11a**−**13a**, and plots of the reaction rate versus pH for **11a** and **13a** are shown in Figure 8. Overall, the activity of these complexes is roughly 1 order of magnitude lower than reaction rates observed with a mixture of $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ and 4 equiv of pta (pta = 1,3,5-triaza-7-phosphaadamantane).[28]

However, the rather low activity of these compounds allowed for the direct identification of a ruthenium bicarbonate-hydride complex, and such an intermediate has been previously proposed,[31] but not identified. Treatment of an aqueous solution of ^{13}C-enriched sodium bicarbonate ($NaH^{13}CO_3$ = 0.10 M)

(24) (a) Richter, B.; Deelman, B.-J.; van Koten, G. *J. Mol. Catal. A* **1999**, *145*, 317. (b) de Wolf, E.; Spek, A. L.; Kuipers, B. W. M.; Philipse, A. P.; Meeldijk, J. D.; Bomans, P. H. H.; Frederick, P. M.; Deelman B.-J.; van Koten, G. *Tetrahedron* **2002**, *58*, 3922.

(25) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259.

(26) (a) Joó, F.; Laurenczy, G.; Nádasdi, L.; Elek, J. *J. Chem. Soc., Chem. Commun.* **1999**, 971. (b) Laurenczy, G.; Joó, F.; Nádasdi, L. *Inorg. Chem.* **2000**, *39*, 5083.

(27) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 344.

(28) Horváth, H.; Laurenczy, G.; Kathó, Á. *J. Organomet. Chem.* **2004**, *689*, 1036.

(29) (a) Kovács, G.; Nádasdi, L.; Joó, F.; Laurenczy, G. *C. R. Acad. Sci., Ser. IIc: Chim.* **2000**, *3*, 601. (b) Kovács, G.; Nádasdi, L.; Laurenczy, G.; Joó, F. *Green Chem.* **2003**, *5*, 213.

(30) Joó, F.; Kovács, J.; Bényei, A. C.; Nádasdi, L.; Laurenczy, G. *Chem. Eur. J.* **2001**, *7*, 193.

(31) Elek, J.; Nádasdi, L.; Papp, G.; Laurenczy, G.; Joó, F. *Appl. Catal. A* **2003**, *255*, 59.

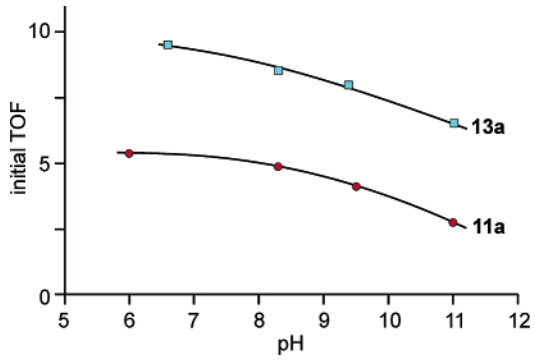
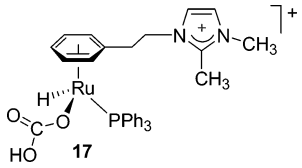


Figure 8. Effect of pH on the CO_2/bicarbonate hydrogenation showing the variation of initial turnover frequency with pH for compounds **11a** and **13a**.

containing the complex **12a** (0.0011 M) with hydrogen (100 bar) at a temperature of 333 K gives rise to a new species, which on the basis of the NMR data is tentatively assigned to complex **17** (unambiguous distinction between a carbonate and bicarbonate species is not possible from the available data).



In the ^{13}C NMR spectrum a doublet is observed at 166.0 ppm ($^3J_{PC}$ = 2.4 Hz), which decreases in intensity as the reaction proceeds. Accordingly, the $^{31}P\{^1H\}$ NMR spectrum displays a doublet at 35.7 ppm (carbonate−phosphine coupling), and the presence of a hydride ligand is confirmed by the ^1H NMR spectrum, showing a doublet at −8.25 ppm ($^2J_{PH}$ = 42 Hz); see Figure 7b and 7c. It is therefore reasonable to assume that the reduction of CO_2 takes place via a bicarbonate species such as **17** with the rate-determining step likely to be the intramolecular hydride transfer from the metal to the complexed bicarbonate, affording formate and water (note that during the catalytic runs no Ru-formate complexes were detected).

Conclusions

A range of ruthenium complexes bearing imidazolium-functionalized η^6-arene ligands have been prepared and their utility in biphasic ionic liquids and aqueous catalysis demonstrated in the hydrogenation of styrene and CO_2. The presence of an imidazolium tag renders these compounds highly water-soluble, even if a lipophilic ligand such as tricyclohexyl phosphine is present. While the activity of some of these compounds in aqueous CO_2 reduction is low, a likely intermediate in the catalytic reaction could be identified by medium-pressure NMR studies. The main advantage of the imidazolium-functionalized arene ruthenium(II) complexes lies in the fact that they can be derivatized with a large range of phosphines and other ligands. While tertiary phosphines were used in this study, we previously reported the derivatization with chiral amino alcohol and diamine ligands. One can envisage that chiral bisphosphines, carbenes, and many other ligands could be employed to give a wide range of compounds with applications in biphasic catalysis, since the coordinated arene provides flexibility in terms of imparting the desired solubility properties, with the subsequent ligand imposing the required catalytic component.

Experimental Section

General Procedures. All synthetic manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and degassed by passing through columns (Innovative Technology) containing molecular sieves and copper (Et_2O, CH_2Cl_2, toluene), distilled from calcium hydride (acetonitrile, DMF, 1,2-dichloroethane) or magnesium (MeOH, EtOH). Doubly distilled water was used in the hydrogenation reactions. The ionic liquid $[C_2pic][Tf_2N]$[32] and compounds **1** and **3b** were prepared as described previously;[10] all other chemicals are commercial products and were used as received. NMR spectra were recorded on a Bruker Avance 400 with chemical shifts δ given in ppm (internal lock as reference) and coupling constants J given in Hz as positive values regardless of their real individual signs. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument according to a literature method,[33] and elementary analyses were carried out at the EPFL.

Synthesis of 2a. A solution of **1** (1.0 g, 7.0 mmol) and 1-methylimidazole (1.15 g, 14.0 mmol) in toluene (1.5 mL) was stirred in an ampule at 110 °C for 24 h, resulting in the formation of two phases. The solvent was removed under vacuum and the residue washed with diethyl ether (2 × 20 mL) to afford **2a** as a white hygroscopic solid. Yield: 1.39 g (88%). ^1H NMR ($CDCl_3$, 400 MHz): 10.27 (s, H^9), 7.52 ($H^{10/11}$), 7.39 ($H^{10/11}$), 5.46 (br, 2H, $H^{4,5}$), 4.26 (m, 2H, H^8), 3.90 (s, 3H, H^{12}), 2.50−2.43 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): 137.2 (C^9), 129.1 (C^1), 123.5 ($C^{10/11}$), 123.1 ($C^{4,5}$), 122.5 (C^2), 121.7 ($C^{10/11}$), 47.3 (C^8), 37.4 (C^7), 36.1 (C^{12}), 28.1 ($C^{3/6}$), 26.2 ($C^{3/6}$). ESI-MS (MeOH): 189.2 $[M]^+$.

Synthesis of 3a. A solution of **1** (500 mg, 3.5 mmol) and 1,2-dimethylimidazole (675 mg, 7.0 mmol) in toluene (1.5 mL) was stirred in an ampule at 110 °C for 24 h, resulting in the formation of a white precipitate. The solvent was removed under vacuum and the residue washed with diethyl ether (2 × 5 mL) to afford **3a** as a white hygroscopic solid. Yield: 0.77 g (92%). ^1H NMR ($CDCl_3$, 400 MHz): 7.81 (d, $^3J_{HH}$ = 2.20, 1H), 7.54 (d, $^3J_{HH}$ = 2.1, 1H), 5.59 (br, 2H, H,[4] H^5), 5.24 (br, H^2), 4.28 (t, $^3J_{HH}$ = 6.9, 2H, H^8), 3.95 (s, 3H, H^{12}), 2.96 (s, 3H, H^{13}), 2.60−2.50 (m, 4H, $H^{3,6}$), 2.39 (d, $^3J_{HH}$ = 6.8, 2H, H^7). ^{13}C NMR ($CDCl_3$, 100 MHz): 143.6 (C^9), 129.4 (C^1), 123.9, 123.3, 123.0, 121.1, 46.8 (C^8), 37.5, 35.7, 28.5, 26.5, 10.2. ESI-MS (MeOH): 203.2 $[M]^+$.

Synthesis of 3c. A solution of **3a** (300 mg, 1.26 mmol) in methylene chloride (20 mL) was treated with $Na[BPh_4]$ (442 mg, 1.26 mmol) and the mixture stirred at ambient temperature for 24 h, during which time a precipitate of NaCl forms. The mixture was filtered, the solution washed with water (2 mL), and the solvent removed in vacuo to afford **3c** as white solid. Yield: 0.56 g (86%). ^1H NMR (CD_2Cl_2, 400 MHz): 7.42 (br, 8H), 7.04 (dd, $^3J_{HH}$ = 7.5,$^3J_{HH}$ = 7.2, 8H), 6.89 (t, $^3J_{HH}$ = 7.2, 4H), 6.50 (1H, H^{10}), 6.41 (1H, H^{11}), 5.75 (br, 2H, H,[4] H^5), 5.26 (br, H^2), 3.62 (t, $^3J_{HH}$ = 7.0, 2H, H^8), 3.06 (s, 3H, H^{12}), 2.67−2.58 (m, 4H, H^3, H^6), 2.22 (t, $^3J_{HH}$ = 6.8, 2H, H^7), 1.87 (s, 3H, H^{13}). ^{13}C NMR (CD_2Cl_2, 100 MHz): 143.3 (C^9), 135.9 (q, $^3J_{BC}$ = 1), 129.2 (C^1), 125.7 (q, $^2J_{BC}$ = 3), 124.1 (C,[4] C^5), 123.4 (C^2), 123.2 (C,[4] C^5), 122.2 (C^{11}), 121.8, 120.6 (C^{10}), 46.5 (C^8), 37.2 (C^2), 34.9 (C^{12}), 28.6 (C^6/C^3), 26.6 (C^6/C^3), 8.89 (C^{13}). Anal. Calcd for $C_{37}H_{39}BN_2$ (522.53 $^g/_{mol}$): C, 85.05; H, 7.52; N, 5.36. Found: C, 85.10; H, 7.37; N, 5.08.

Synthesis of 4a. A solution of **1** (2.0 g, 1.4 mmol) and 1-butylimidazole (8.7 g, 7.0 mmol) in toluene (5 mL) was stirred in an ampule at 110 °C for 10 h, resulting in the formation of a second layer. The solvent was removed under vacuum and the residue washed with diethyl ether (2 × 10 mL) to afford **4a** as a white solid. Yield: 3.37 g (90%). ^1H NMR ($CDCl_3$, 400 MHz): 10.62 (s, H^9), 7.49 (s, $H^{10,11}$), 5.61 (m, $H^{4,5}$), 5.39 (br, H^2), 4.46 (t,

(32) Wasserscheid, P.; Metlen, A.; Brausch, Patent WO2005014547, N.; 2005.

(33) Dyson, P. J.; McIndoe, J. S. *Inorg. Chim. Acta* **2003**, *354*, 68.

$^3J_{HH}$ = 7.0, 2H, H^8), 4.29 (t, $^3J_{HH}$ = 7.2, 2H, H^{12}), 2.65−2.55 (m, 6H), 1.84 (tt, 2H, H^{13}), 1.29 (qt, 2H, H^{14}), 0.90 (t, $^3J_{HH}$ = 7.3, 2H, H^{15}). ^{13}C NMR ($CDCl_3$, 100 MHz): 137.6 (C^9), 129.4 (C^1), 123.8 ($C^{4/5}$), 123.6 ($C^{4/5}$), 122.2 (C^{10}), 121.8 (C^{11}), 49.7 (C^{12}), 47.7 (C^8), 37.9 ($C^{3/6}$), 32.1 (C^{13}), 28.4 ($C^{3/6}$), 26.6 (C^7), 19.3 (C^{14}), 13.4 (C^{15}). ESI-MS (MeOH): 231.2 $[M]^+$.

Synthesis of 5a. To a solution of **2a** (1.43 g, 6.4 mmol) in methanol (20 mL) was added $RuCl_3 \cdot 3H_2O$ (450 mg, 1.7 mmol) and the mixture stirred at 80 °C for 20 h, during which time an orange solid precipitated. The mixture was filtered and the residue washed with ethanol (2 × 5 mL) to afford **5a** as orange solid. Yield: 0.66 g (97%). ^{1}H NMR (d_6-DMSO, 400 MHz): 9.29 (s, H^9), 7.80 (s, H^{10}), 7.75, (s, H^{11}), 6.04 (m, $H^{3,5}$), 5.88 (d, $^3J_{HH}$ = 5.9, 2H, $H^{2,6}$), 5.85 (t, $^3J_{HH}$ = 5.6, 1H, H^4), 4.57 (t, $^3J_{HH}$ = 7.0, H^8), 3.85 (s, H^{12}) 3.00 (t, $^3J_{HH}$ = 7.0, H^7). ^{13}C NMR (d_6-DMSO, 100 MHz): 137.5 (C^9), 124.2 (C^{10}), 122.8 (C^{11}), 101.6 (C^1), 88.8 ($C^{3,5}$), 87.0 ($C^{2,6}$), 85.1 (C^4), 48.4 (C^8), 36.5 (C^{12}), 33.9 (C^7). ESI-MS (H_2O): 359.2 $[Monomer]^+$. Anal. Calcd for $C_{24}H_{30}Cl_6N_4Ru_2 \cdot H_2O$: C, 35.70; H, 3.99, N: 6.94. Found: C, 35.78; H, 4.08; N, 6.97.

Synthesis of 6a. A suspension of $RuCl_3 \cdot 3H_2O$ (220 mg, 0.88 mmol) and **3a** (800 mg, 3.4 mmol) in methanol (10 mL) was stirred at 80 °C for 20 h, during which time an orange solid precipitated. The mixture was filtered and the residue washed with ethanol (2 × 5 mL) to afford **6a** as orange solid. Yield: 345 mg (96%). ^{1}H NMR (d_6-DMSO, 400 MHz): 7.65 (br, H,[10] H^{11}), 6.03 (m, $H^{3,5}$), 5.96 (d, $^3J_{HH}$ = 6.0, 2H, $H^{2,6}$), 5.87 (m, H^4), 4.53 (t, $^3J_{HH}$ = 7.2, H^8), 3.76 (s, H^{12}) 2.91 (t, $^3J_{HH}$ = 7.2, H^7), 2.62 (s, H^{13}). ^{13}C NMR (d_6-DMSO, 100 MHz): 145.1 (C^9), 123.0 (C^{11}), 121.4 (C^{10}), 101.3 (C^1), 88.5 ($C^{3,5}$), 87.3 ($C^{2,6}$), 85.3 (C^4), 46.9 (C^8), 35.3 (C^{12}), 33.3 (C^7), 10.0 (C^{13}). ESI-MS (H_2O): 372.9 $[Monomer]^+$. Anal. Calcd for $C_{26}H_{34}Cl_6N_4Ru_2$: C, 38.20; H, 4.19; N, 6.85. Found: C, 38.03; H, 4.17; N, 6.64.

Synthesis of 7a. A solution of $RuCl_3 \cdot 3H_2O$ (900 mg, 3.4 mmol) and **4a** (3.4 g, 12.7 mmol) in methanol (100 mL) was stirred at 80 °C for 8 h, after which time the hot solution was filtered and the solvent removed in vacuo. The crude product was washed with ethanol (2 × 5 mL) to remove excess diene, affording **7a** as an orange solid. Yield: 1.35 g (90%). ^{1}H NMR (d_6-DMSO, 400 MHz): 9.28 (s, 1H, H^9), 7.81 (br, 2H, $H^{10,11}$), 6.03 (t, $^3J_{HH}$ = 6.0, 2H, $H^{3,5}$), 5.85 (m, 3H, $H^{2,4,6}$), 4.56 (t, $^3J_{HH}$ = 7.1, 2H, H^8), 4.15 (t, $^3J_{HH}$ = 7.1, 2H, H^{12}), 3.01 (t, $^3J_{HH}$ = 7.1, 2H, H^7), 1.75 (tt, 2H, H^{13}), 1.18 (qt, 2H, H^{14}), 0.88 (t, $^3J_{HH}$ = 7.3, 3H, H^{15}). ^{13}C NMR (d_6-DMSO, 100 MHz): 136.7 (C^9), 123.1 (C^{10}), 123.0 (C^{11}), 101.7 (C^1), 88.8 ($C^{3,5}$), 86.8 ($C^{2,6}$), 85.0 (C^4), 49.1 (C^{12}), 48.4 (C^8), 33.7 (C^7), 31.6 (C^{13}), 19.2 (C^{14}), 13.7 (C^{15}). ESI-MS (MeOH): 400.8 $[M - Cl]^+$. Anal. Calcd for $C_{30}H_{42}Cl_6N_4Ru_2 \cdot H_2O$: C, 40.42; H, 4.97; N, 6.28. Found: C, 40.68; H, 4.83; N, 6.29.

Synthesis of 8. To a solution of $RuCl_3 \cdot 3H_2O$ (200 mg, 0.76 mmol) in ethanol (5 mL) was added 1-(2-chloroethyl)cyclohexa-1,4-diene, **1** (440 mg, 3.0 mmol), and the solution stirred for 18 h in an ampule at 75 °C, resulting in an orange precipitate and an almost colorless solvent phase. The product was collected via filtration and washed with diethyl ether (2 × 5 mL) to almost quantitatively afford **8** as an orange-red solid. Yield: 235 mg (98%). ^{1}H NMR (d_6-DMSO, 400 MHz): 6.02 (m, 2H, $H^{3,5}$), 5.92 (d, $^3J_{HH}$ = 6.1, 2H, $H^{2,6}$), 5.83 (t, $^3J_{HH}$ = 5.6, 1H, H^4), 3.97 (t, $^3J_{HH}$ = 6.7, 2H, H^8), 2.90 (d, $^3J_{HH}$ = 6.7, 2H, H^7). ^{13}C NMR (d_6-DMSO, 100 MHz): 102.6 (C^1), 88.5 ($C^{3,5}$), 87.2 ($C^{2,6}$), 85.1 (C^4), 43.9 (C^8), 35.9 (C^7). ESI-MS ($CHCl_3$): 588.6 $[M - Cl]^+$. Anal. Calcd for $C_{16}H_{18}Cl_6Ru_2$: C, 30.74; H, 2.90. Found: C, 31.11; H, 2.94.

Synthesis of 9. To a suspension of **8** (100 mg, 0.16 mmol) in toluene (5 mL) was added 1-methylimidazole (76 μL, 0.96 mmol) and the mixture stirred in an ampule at 110 °C for 24 h, resulting in the precipitation of a bright yellow solid and a colorless solvent phase. The solid was isolated via filtration and washed with diethyl ether (2 × 5 mL) to afford **9** as a yellow solid. Yield: 145 mg (95%). ^{1}H NMR ($CDCl_3$, 400 MHz): 9.09 (s, 2H, H^9), 7.52 (br, 2H), 6.78 (br, 2H), 6.01 (m, 3H), 5.76 (m, 2H), 3.75 (m, 8H, $H^{8,12}$), 2.78 (t, $^3J_{HH}$ = 6.3, 2H, H^7). ^{13}C NMR ($CDCl_3$, 100 MHz): 142.2 (C^9), 131.0, 120.7, 99.8 (C^1), 87.4, 83.8, 82.4 (C^4), 43.1 (C^8), 35.9 (C^7), 34.7 (C^{12}). ESI-MS (MeOH): 440.9 $[M]^+$, 359.0 $[M - Imidazole]^+$, 277.0 $[M - 2\ Imidazole]^+$. Anal. Calcd for $C_{16}H_{21}Cl_3N_4Ru$: C, 40.31; H, 4.44; N, 11.75. Found: C, 39.60; H, 4.57; N, 11.57.

Synthesis of 10. A solution of **9** (45 mg, 0.09 mmol) in *N*-methylimidazole (1 mL) was stirred in an ampule at 110 °C for 18 h, resulting in an orange-red solution. Some of the excess imidazole was removed in vacuo and then diethyl ether (10 mL) added, resulting in the precipitation of an orange-red solid, which was further washed with diethyl ether (5 mL) to afford the product. Yield: 46 mg (74%). ^{1}H NMR (D_2O, 400 MHz): 7.00 (s, 6H), 6.85 (br, 6H), 6.33 (s, 6H), 3.60 (s, 18H, CH_3). ^{13}C NMR (D_2O, 100 MHz): 141.3, 130.9, 122.3, 33.6. ESI-MS (MeOH): 628.9 $[M + Cl]^+$, 546.7 $[M + Cl - Imidazole]^+$, 382.9, $[RuCl(imidazole)_3]^+$. Anal. Calcd for $C_{24}H_{36}Cl_2N_{12}Ru \cdot H_2O$: C, 42.23; H, 5.61; N, 24.62. Found: C, 41.02; H, 5.88; N, 25.08.

Synthesis of 11a. To a suspension of **5a** (87 mg, 0.11 mmol) in methanol/dichloromethane, 1:1 (8 mL), was added triphenylphosphine (58 mg, 0.22 mmol) and the mixture stirred at RT for 1 h, affording a red solution. The solvent was removed and the residue washed with diethyl ether (2 × 2 mL). Yield: 142 mg (98%). ^{1}H NMR ($CDCl_3$, 400 MHz): 9.95 (br, H^9), 8.08 (s, H^{11}), 7.76 (m, 6H), 7.41 (m, 9H), 7.20 (s, H^{10}), 5.88 (m, 2H, $H^{2,6}$), 5.14 (br, 2H, $H^{3,5}$), 4.94 (br, 2H, H^8), 4.44 (br, H^4), 3.82 (s, 3H, H^{12}), 3.41 (br, 2H, H^7); (d_6-DMSO, 400 MHz): 9.19 (s, 1H, H^9), 7.76 (s, 1H, H^{10}), 7.70 (s, 1H, H^{11}), 7.63 (m, 6H), 7.45 (m, 9H), 5.50 (d, $^2J_{HH}$ = 5.3, 2H, $H^{2,6}$), 5.36 (m, 2H, $H^{3,5}$), 4.83 (br, H^4), 4.56 (t, $^2J_{HH}$ = 6.7, 2H, H^8), 3.84 (s, 3H, H^{12}), 3.01 (t, $^2J_{HH}$ = 6.7, 2H, H^7). ^{13}C NMR ($CDCl_3$, 100 MHz): 139.2 (C^9), 134.3 (d, $^3J_{CP}$ = 9), 133.1 (d, $^1J_{CP}$ = 48), 130.7, 128.3 (d, $^2J_{CP}$ = 10), 124.2 (C^{11}), 123.0 (C^{10}), 107.7 (C^1), 89.6 ($C^{2,6}$), 87.5 ($C^{3,5}$), 82.4 (C^4), 48.3 (C^8), 37.1 (C^{12}), 33.7 (C^7); (d_6-DMSO): 137.3 (C^9), 134.4 (d, $^3J_{CP}$ = 9), 133.1 (d, $^1J_{CP}$ = 48), 130.8, 128.5 (d, $^2J_{CP}$ = 10), 124.2 (C^{11}), 122.8 (C^{10}), 106.3 (d, $^2J_{PC}$ = 7, C^1), 89.1 (d, $^2J_{PC}$ = 5, $C^{2,6}$), 88.7 ($C^{3,5}$), 82.4 (C^4), 48.0 (C^8), 36.3 (C^{12}), 33.6 (C^7). ^{31}P NMR ($CDCl_3$): 29.4 (s); (d_6-DMSO, 162 MHz): 28.3 (s). ESI-MS (CH_2Cl_2): 620.9 $[M]^+$. Anal. Calcd for $C_{30}H_{30}Cl_3N_2PRu \cdot 1/2CH_2Cl_2$: C, 52.37; H, 4.47; N, 4.01. Found: C, 52.30; H, 4.90; N, 3.92.

Synthesis of 12a. To a suspension of **6a** (100 mg, 0.125 mmol) in methanol/1,2-dichloroethane, 1:1 (10 mL), was added triphenylphosphine (65 mg, 0.25 mmol) and the mixture stirred at RT for 1 h, affording an almost clear solution. The mixture was filtered, the solvent removed under vacuum, and the residue washed with diethyl ether (2 × 2 mL), affording the product as a red-orange solid. Yield: 152 mg (91%). ^{1}H NMR ($CDCl_3$, 400 MHz): 8.22 (s, H^{11}) 7.68 (m, 6H), 7.47 (s, H^{10}), 7.42 (m. 9H), 5.86 (d, $^3J_{HH}$ = 5.7, 2H, $H^{2,6}$), 5.09 (br, 2H, $H^{3,5}$), 4.99 (t, $^3J_{HH}$ = 7.4, 2H, H^8), 4.54 (m, 1H, H^4), 3.84 (s, 3H, H^{12}), 3.29 (br, 2H, H^7), 2.86 (s,3H, H^{13}). (d_6-DMSO, 400 MHz): 7.63 (m, 8H), 7.47 (m. 9H), 5.57 (d, $^3J_{HH}$ = 5.5, 2H, $H^{2,6}$), 5.37 (br, 2H, $H^{3,5}$), 4.87 (br, 1H, H^4), 4.51 (br, 2H, H^8), 3.75 (s, 3H, H^{12}), 2.90 (br, 2H, H^7), 2.60 (s, 3H, H^{13}). ^{13}C NMR ($CDCl_3$, 100 MHz): 144.3 (C^9), 134.2 (d, $^2J_{PC}$ = 9), 133.1 (d, $^1J_{PC}$ = 47), 130.6 (d, $^4J_{PC}$ = 2), 128.3 (d, $^3J_{PC}$ = 10), 122.7 (C^{11}), 122.6 (C^{10}), 106.6 (d, $^2J_{PC}$ = 9, C^1), 90.4 (d, $^2J_{PC}$ = 5, $C^{2,6}$), 86.8 ($C^{3,5}$), 82.5 (C^4), 46.7 (C^8), 35.8 (C^{12}), 33.8 (C^7), 11.1 (C^{13}); (d_6-DMSO, 100 MHz): 145.1 (C^9), 134.4 (d, $^2J_{PC}$ = 9), 133.1 (d, $^1J_{PC}$ = 47), 130.8, 128.6 (d, $^3J_{PC}$ = 10), 123.0 (C^{11}), 121.3 (C^{10}), 105.8 (d, $^2J_{PC}$ = 7, C^1), 89.4 (d, $^2J_{PC}$ = 6, $C^{2,6}$), 88.7 ($C^{3,5}$), 82.4 (C^4), 46.7 (C^8), 35.3 (C^{12}), 33.2 (C^7), 9.9 (C^{13}). ^{31}P NMR ($CDCl_3$, 162 MHz): 28.7 (s). (d_6-DMSO, 162 MHz): 28.1 (s). ESI-MS (MeOH): 653.0 $[M]^+$. Anal. Calcd for $C_{31}H_{32}Cl_3N_2PRu \cdot H_2O$: C, 54.04; H, 4.97; N, 4.07. Found: C, 54.04; H, 5.00; N, 3.97.

Table 4. Crystallographic Data for 3c, 11c, 12d, 14c, and 16

	3c	11c	12d	14c	16
formula	$C_{37}H_{39}BN_2$	$C_{54}H_{50}BCl_2N_2PRu$	$C_{66}H_{70}Cl_8N_6P_2PdRu_2$	$C_{57}H_{56}BCl_2N_2PRu$	$C_{15}H_{20}Cl_2N_2Ru$
M	522.51	940.71	1601.36	982.79	400.30
T [K]	140(2)	293(2)	140(2)	140(2)	140(2)
cryst syst	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [Å]	9.653(4)	10.0450(17)	9.2984(15)	9.8915(4)	8.4686(8)
b [Å]	30.884(10)	14.974(3)	9.7207(18)	28.6704(16)	8.6857(11)
c [Å]	10.1847(8)	16.593(4)	20.453(3)	17.3285(11)	10.8580(11)
α [deg]	90.0	107.298(19)	86.374(14)	90.0	76.064(10)
β [deg]	97.648(16)	101.259(17)	87.931(13)	100.768(5)	87.346(8)
γ [deg]	90.0	99.948(16)	64.960(16)	90.0	84.323(9)
V [Å^3]	3009.2(15)	2264.9(8)	1671.5(5)	4827.7(5)	771.15(14)
Z	4	2	1	4	2
density [Mg/m^3]	1.153	1.379	1.591	1.352	1.724
μ [mm^{-1}]	0.066	0.539	1.125	0.509	1.354
2θ range [deg]	$2.91 \le 2\theta \le 25.03$	$3.18 \le 2\theta \le 25.02$	$2.98 \le 2\theta \le 25.03$	$3.08 \le 2\theta \le 25.03$	$3.44 \le 2\theta \le 25.03$
no. of reflns collected	17 799	8809	10 135	27 660	4520
no. of indep reflns	5048 [$R_{int} = 0.0588$]	5738 [$R_{int} = 0.0734$]	5149 [$R_{int} = 0.0910$]	8158 [$R_{int} = 0.0520$]	2379 [$R_{int} = 0.0360$]
GooF on F^2	1.093	0.903	0.779	1.050	1.107
final R_1, wR_2 [$I > 2\sigma(I)$]	0.0686, 0.1593	0.0596, 0.1415	0.0554, 0.1103	0.0461, 0.1082	0.0346, 0.0908

Synthesis of 12d. To a solution of **12a** (60 mg, 0.09 mmol) in acetonitrile (5 mL) was added palladium dichloride (8 mg, 0.045 mmol) and the mixture stirred at RT for 18 h, affording an orange precipitate. The solvent was removed under vacuum and the remaining solid washed with dichloromethane (2 × 2 mL) to afford the product as an orange powder. Yield: 62 mg (92%). ^{1}H NMR (d_6-DMSO, 400 MHz): 7.68−7.40 (m, 17 H), 5.56 (d, $^3J_{HH} = 6.4$, H^{2,6}), 5.37 (dd, $^3J_{HH} = 6.4$, $^3J_{HH} = 5.4$, H^{3,5}), 4.88 (t, $^3J_{HH} = 5.4$, H^4), 4.50 (t, $^3J_{HH} = 7.6$, H^8), 3.74 (s, H^{12}), 2.90 (t, $^3J_{HH} = 7.6$, H^7), 2.59 (s, H^{13}). ^{13}C NMR (d_6-DMSO, 100 MHz): 145.1 (C^9), 134.4 (d, $^3J_{CP} = 9$), 133.9 (d, $^1J_{CP} = 46$), 130.8, 128.5 (d, $^2J_{CP} = 10$), 123.0 (C^{10}), 121.3 (C^{11}), 105.8 (d, $^2J_{CP} = 7$, C^1), 89.5 (d, $^2J_{CP} = 6$, C^{2,6}), 88.6 (C^{3,5}), 82.4 (C^4), 46.7 (C^8), 35.2 (C^{12}), 33.2 (C^7), 9.8 (C^{13}). ^{31}P NMR (d_6-DMSO, 162 MHz): 28.1 (s). ESI-MS (CH_3-CN): 704.9 [M + Cl]$^-$; 634.9 [M − Cl]$^+$; 213.2 [$PdCl_3$]$^-$. Anal. Calcd for $C_{62}H_{64}Cl_8N_4P_2PdRu_2 \cdot CH_2Cl_2$: C, 47.17; H, 4.15; N, 3.49. Found: C, 47.08; H, 4.14; N, 3.34.

Synthesis of 13a. To a suspension of **6a** (200 mg, 0.25 mmol) in DMF (20 mL) was added tricyclohexylphosphine (138 mg, 0.50 mmol) and the mixture stirred at 50 °C for 1 h, during which time the color darkened. The mixture was filtered, the solvent removed under vacuum, and the residue washed with diethyl ether (2 × 5 mL) to remove excess phosphine, affording the product as a brown solid. Yield: 305 mg (90%). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.90 (H^{11}), 7.47 (H^{10}), 5.71 (br, H^{2,6}), 5.57 (br, H^4), 5.53 (br, H^{3,5}), 4.89 (br, H^8), 3.90 (H^{12}), 3.20 (br, H^7), 2.82 (s, H^{13}), 2.43 (dd, 3H), 2.09 (6H), 1.81 (6H), 1.74 (6H), 1.43 (6H), 1.28 (6H). ^{13}C NMR ($CDCl_3$, 100 MHz): 144.3 (C^9), 123.9 (C^{11}), 123.7 (C^{10}), 106.3 (C^1), 90.7 (C^{2,6}), 83.0 (C^{3,5}), 78.1 (C^4), 47.9 (C^8), 37.6 (C^{12}), 33.5 (C^7), 36.0 (d, $^2J_{PC} = 19$), 29.9, 27.6 (d, $^3J_{PC} = 10$), 26.4. ^{31}P NMR ($CDCl_3$, 162 MHz): 31.8 (s). ESI-MS: 653.2 [M]$^+$, 375.1 [M − PCy_3]$^+$. Anal. Calcd for $C_{31}H_{50}Cl_3N_2PRu \cdot H_2O$: C, 52.65; H, 7.41; N, 3.96. Found: C, 52.56; H, 7.60; N, 3.69.

Synthesis of 14a. To a suspension of **7a** (250 mg, 0.29 mmol) in methanol/dichloromethane, 1:1 (15 mL), was added triphenyl phosphine (150 mg, 0.58 mmol) and the mixture stirred at RT for 1 h, affording a red solution. The solvent was removed and the residue washed with diethyl ether (2 × 5 mL). Yield: 384 mg (96%). ^{1}H NMR ($CDCl_3$, 400 MHz): 10.21 (s, 1H, H^9), 8.10 (s, 1H, H^{11}), 7.68 (dt, 6H), 7.42 (m, 9H), 7.10 (s, 1H, H^{10}), 5.84 (d, $^3J_{HH} = 5.6$, 2H, H^{2,6}), 5.14 (dt, 2H, H^{3,5}), 4.98 (br, 2H, H^8), 4.41 (br, 1H, H^4), 4.09 (t, $^3J_{HH} = 7.3$, 2H, H^{12}), 3.46 (t, 2H, H^7), 1.80 (tt, 2H, H^{13}), 1.29 (qt, 2H, H^{14}), 0.93 (t, $^3J_{HH} = 7.2$, 3H, H^{15}). ^{13}C NMR ($CDCl_3$, 100 MHz): 137.9 (C^9), 134.2 (d, $^2J_{PC} = 9$), 133.0 (d, $^1J_{PC} = 48$), 130.6 (d, $^4J_{PC} = 2$), 128.3 (d, $^3J_{PC} = 10$), 124.2 (C^{11}), 121.1 (C^{10}), 107.9 (d, $^2J_{PC} = 8$, C^1), 89.4 (d, $^2J_{PC} = 5$, C^{2,6}), 87.5 (C^{3,5}), 82.4 (C^4), 49.9 (C^{12}), 48.0 (C^8), 33.4 (C^7), 31.9 (C^{13}), 19.5 (C^{14}), 13.5 (C^{15}). ^{31}P NMR ($CDCl_3$, 162 MHz): 29.5 (s). ESI-MS (MeOH): 662.9 [M]$^+$. Anal. Calcd for $C_{33}H_{36}Cl_3N_2PRu \cdot H_2O$: C, 55.27; H, 5.24; N, 3.91. Found: C, 55.03; H, 5.30; N, 3.70.

Synthesis of 14d. To a solution of **14a** (158 mg, 0.025 mmol) in acetonitrile (15 mL) was added palladium dichloride (20 mg, 0.011 mmol) and the mixture stirred at RT for 18 h, affording an orange precipitate. The solution was concentrated and filtered and the residue washed with diethyl ether (2 × 5 mL). Yield: 144 mg (81%). ^{1}H NMR (d_6-DMSO, 400 MHz): 9.22 (s, 1H, H^9), 7.79 (s, 2H, H^{10,11}), 7.62 (m, 6H), 7.50−7.40 (m, 9H), 5.46 (d, $^3J_{HH} = 5.9$, 2H, H^{2,6}), 5.25 (m, 2H, H^{3,5}), 4.85 (t, br, 1H, H^4), 4.57 (t, $^3J_{HH} = 7.0$, 2H, H^8), 4.14 (t, $^3J_{HH} = 7.0$, 2H, H^{12}), 3.03 (t, $^3J_{HH} = 7.0$, 2H, H^7), 1.73 (tt, 2H, H^{13}), 1.17 (qt, 2H, H^{14}), 0.87 (t, $^3J_{HH} = 7.0$, 3H, H^{15}). ^{13}C NMR (d_6-DMSO, 100 MHz): 136.7 (C^9), 134.4 (d, $^3J_{CP} = 9$), 133.1 (d, $^1J_{CP} = 48$), 130.8, 128.5 (d, $^2J_{CP} = 10$), 123.1 (C^{10}), 123.0 (C^{11}), 106.2 (d, $^2J_{PC} = 7$, C^1), 89.1 (d, $^2J_{PC} = 6$, C^{2,6}), 88.7 (C^{3,5}), 82.4 (C^4), 49.1 (C^{12}), 48.2 (C^8), 33.5 (C^7), 31.6 (C^{13}), 19.2 (C^{14}), 13.7 (C^{15}). ^{31}P NMR (d_6-DMSO, 162 MHz): 28.4 (s). ESI-MS (MeOH): 662.9 [M]$^+$. Anal. Calcd for $C_{66}H_{72}Cl_8N_4P_2PdRu_2 \cdot 1/2CH_2Cl_2$: C, 49.37; H, 4.55; N, 3.46. Found: C, 49.21; H, 4.67; N, 3.38.

Synthesis of 16. A solution of **7a** (200 mg, 0.23 mmol) in DMF (100 mL) was stirred for 12 h at RT, then the solvent was removed in vacuo and the residue redissolved in dichloromethane (50 mL). The solution was filtered and silver oxide (53 mg, 0.23 mmol) added. The mixture was stirred for 18 h, then filtered through Celite to remove AgCl. The remaining solution was concentrated, then diethyl ether added to precipitate the product. Complex **16** was obtained as an orange-brown solid; yield 115 mg (63%). ^{1}H NMR (CD_2Cl_2, 400 MHz): 7.20 (s, H^{11}), 6.99 (s, H^{10}), 6.04 (t, $^3J_{HH} = 6.0$, H^4), 5.74 (dd, $^3J_{HH} = 6.0$, $^3J_{HH} = 5.6$, H^{3,5}), 5.20 (d, $^3J_{HH} = 5.6$, H^{2,6}), 4.48 (t, $^3J_{HH} = 5.5$, H^8), 4.30 (t, $^3J_{HH} = 7.9$, H^{12}), 2.76 (t, $^3J_{HH} = 5.5$, H^7), 1.64 (tt, H^{13}), 1.31 (qt, H^{14}), 0.92 (t, $^3J_{HH} = 7.3$, H^{15}). ^{13}C NMR (CD_2Cl_2, 100 MHz): 167.8 (C^9), 122.4 (C^{11}), 121.9 (C^{10}), 94.7 (C^{3,5}), 90.8 (C^4), 91.1 (C^1), 78.5 (C^{2,6}), 50.9 (C^8), 50.8 (C^{12}), 34.3 (C^{13}), 29.9 (C^7), 19.7 (C^{14}), 13.7 (C^{15}). ESI-MS (MeOH): 365.0 [M − Cl]$^+$, 329.1 [M − 2Cl]$^+$.

Crystallography. Data collection for the X-ray structure determinations was performed on a mar345 (**3c**) or an a KUMA CCD diffractometer system using graphite-monochromated Mo Kα (0.71070 Å) radiation and a low-temperature device [$T = 140(2)$ K]. Crystals suitable for X-ray diffraction studies of **3c**, **11c**, **14c**, and **16** were grown from slow diffusion of diethyl ether into CH_2Cl_2 solutions, respectively; those of **12d**, from slow diffusion of diethyl ether into a CH_3CN solution. Data reduction was performed

by CrysAlis RED.[34] The structures of **11c** and **12d** were solved with Patterson methods and those of **3c**, **14c**, and **16** with direct methods using SHELX97[35] both for the solution and refinement by successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against F^2). An empirical absorption correction (DELABS)[36] was applied to **11c**, **12d**, **14c**, and **16**. All non-hydrogen atoms were refined anisotropically. In **11c** and **12d** the structure was restrained using the DELU command, and some atoms were further restrained using the ISOR command. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Relevant crystallographic data are compiled in Table 4.

Hydrogenation of Styrene. In a typical reaction a solution of catalyst (0.0087 mmol) in water or ionic liquid [C_2pic][Tf_2N] (1 mL), styrene (8.7 mmol), and cyclohexane (2 mL) were added to a glass vial, and the mixture was stirred at 80 °C under a pressure of 40 bar H_2 for 2 h. The resulting biphasic mixture was extracted twice with Et_2O (2 mL), the upper organic phase decanted, and the conversion of styrene to ethyl benzene determined by GC. The immobilization phase was then recharged with styrene and cyclohexane and the reaction repeated.

Hydrogenation of CO_2. The reactions were carried out in medium-pressure sapphire NMR tubes (pressure <120 bar) and were followed by NMR spectroscopy on a Bruker DRX 400 NMR spectrometer. D_2O (99.9%), D_2 (99.9%), Na_2CO_3 (99%), and $NaHCO_3$ (99%) enriched in ^{13}C were purchased from Cambridge Isotope Laboratories. TSPSA and phosphoric acid were used as references for the ^1H and ^{31}P NMR measurements, respectively. Spectra were fitted with WINNMR and NMRICMA/MATLAB programs on a PC.

In a typical reaction **11a**, **12a**, or **13a** (1.5 mg, 2.2×10^{-6} mol), 2.0×10^{-4} mol ^{13}C-enriched bicarbonate (16.8 mg of $NaHCO_3$) or carbonate (21.4 mg of Na_2CO_3) (or a mixture of both), D_2O (0.7 mL), and H_2O (1.30 mL) were introduced under nitrogen atmosphere into a 10 mm medium-pressure sapphire NMR tube. After dissolution of all solid material, 100 bar of H_2 (and 10 bar of CO_2 where appropriate) was added. The reaction was followed in situ, and the concentrations of HCO_2^-, CO_3^{2-}/HCO_3^-, and CO_2 were determined from integration of the corresponding ^{13}C and ^1H NMR signals. The initial rates and turnover frequencies were calculated by fitting the experimental data from the initial stages of the reaction.

The effect of pH on the hydrogenation of CO_2 was studied as follows. Below pH 8.3, the pH values of the reaction mixtures were determined from the ratio of the integrals of ^{13}C NMR signals of CO_2 and bicarbonate. In the alkaline pH range (8.3−11.0), an appropriate mixture of Na_2CO_3 and $NaHCO_3$ was prepared in order to obtain a solution of the desired pH. In this pH range there is a fast exchange (on the NMR time scale) between carbonate and bicarbonate, and therefore an average ^{13}C NMR shift was determined. A calibration curve of the pH versus chemical shift was prepared, and the actual ^{13}C chemical shift of a CO_3^{2-}/HCO_3^- solution is directly related to its pH.[26b]

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Supporting Information Available: Kinetic data of the CO_2-reduction studies as well as crystallographic information files (CIF) of **3c**, **11c**, **12d**, **14c**, and **16** are available free of charge via the Internet at http://pubs.acs.org.

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