Catalytic Activity of Bis-phosphine Ruthenium(II)−Arene Compounds: Chemoselective Hydrogenation and Mechanistic Insights

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Summary: Bis-phosphine ruthenium(II)−arene complexes have been found to be highly active and chemoselective catalysts for the hydrogenation of aldehydes in the presence of olefinic bonds. Mechanistic studies, including comparisons with a structural analogue, reactions of an isolated hydride complex, base poisoning experiments, and a computational analysis, help rationalize the preferential hydrogenation of C═O bonds, which is suggested to proceed via an ionic outer-sphere mechanism.

Introduction

The catalytic chemoselective reduction of carbonyl groups in the presence of olefinic bonds is a particularly challenging task, since most common catalysts are selective for the reduction of C═C bonds,[1] and the discovery of active catalysts for this process is of ongoing importance. The most successful catalysts for this process are arguably ruthenium-based diamino−bis-phosphine (or diphosphine) complexes, selective for the reduction of ketone and aldehyde groups.[1,2] With these catalysts, C═O bonds in α,β-unsaturated carbonyl compounds can be reduced with a selectivity of >99% with TONs up to 10 000. Other notable examples are ruthenium-$PPh_2(C_6H_4$-3-$SO_3Na)$ or $P(C_6H_4$-3-$SO_3Na)_3$ systems, which show pH-tunable selectivity for the hydrogenation of unsaturated aldehydes under biphasic conditions,[1,3,4] although other catalysts are also known.[1,5] Following earlier work in our group involving the investigation of phosphine dissociation characteristics and prescreening for catalytic activity,[6] we report here the activity of the air- and moisture-stable bis-phosphine ruthenium(II)−arene complexes, $[RuCl(PR_3)(PR'_3)(p\text{-cymene})]PF_6$ (**1a**, R = Ph, P′ = *p*-tol; **1b**, R = R′ = Ph; **1c**, R = R′ = *p*-tol), for the chemoselective reduction of aldehydes together with a mechanistic and computational study.

Results and Discussion

Initial experiments, with styrene, benzaldehyde, and 3-phenylpropionaldehyde as substrates, demonstrated that **1a** is an active precatalyst, with comparable conversions, for the hydrogenation of both C═C and C═O bonds in toluene at 50 °C under 50 bar of H_2 (Table 1). Competition experiments with **1a** indicated, however, a high preference for the hydrogenation of benzaldehyde over styrene (82% C═O selectivity). This selectivity was further confirmed by experiments using **1a** for the hydrogenation of *trans*-cinnamaldehyde, with C═O selectivity approaching 100%. Similar selectivity was observed for **1b** and **1c**, with the activity increasing in the order **1b** > **1a** > **1c**. In base poisoning experiments using NEt_3, carried out to aid mechanistic investigations, benzaldehyde hydrogenation was dramatically reduced, whereas styrene hydrogenation was enhanced. Large decreases in activity and changes in selectivity were also observed for the competition experiment and hydrogenation of *trans*-cinnamaldehyde using **1a**. Furthermore, addition of mercury, a selective poison for heterogeneous catalysis, did not inhibit catalytic activity significantly (Table 1).[7]

In addition to the bis-phosphine complexes **1**, the catalytic activity of a structural analogue, $[Ru(\kappa^2\text{-}PPh_2C_6H_4O)(OCMe_2)(p\text{-cymene})]PF_6$ (**2**),[8] containing instead a more strongly bound anionic chelating P,O ligand and a labile acetone ligand, was determined in an attempt to assess the role of the chloride ligand during catalysis. Complex **2** was prepared by chloride abstraction from $[RuCl(\kappa^2\text{-}PPh_2C_6H_4O)(p\text{-cymene})]$[6] in CH_2Cl_2−acetone with $AgPF_6$ (solid-state structure in Figure 1) and showed similar activity for the hydrogenation of benzaldehyde and 3-phenylpropionaldehyde, but much reduced activity for the hydrogenation of styrene (although in the presence of NEt_3 activity is comparable).[9] Correspondingly, a high C═O selectivity was found for the reduction of *trans*-cinnamaldehyde using **2**.

The reactivity of complex **1b** with H_2 was examined in situ using a high-pressure sapphire NMR tube under similar conditions (i.e., THF, 50 °C, 50 bar of H_2). Formation of the hydride complex, $[RuHCl(PPh_3)(p\text{-cymene})]$ (**3**), presumably following phosphine dissociation and dihydrogen coordination, is observed together with anion hydrolysis and other minor products. Following optimization, **3** was prepared in 66% isolated yield

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(8) Although $[Ru(PPh_3)(\kappa^2\text{-}PPh2C6H4O)(p\text{-cymene})]PF_6$ would be a better model, dissociation of triphenylphosphine is not facile (see ref 6) and instead a labile acetone ligand was used.

(9) In comparison to the bis-phosphine complexes, **2** is significantly air-sensitive and the preparation of catalyst solutions in a glovebox was required.

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Table 1. Catalytic Activity of 1 and 2[a]

	substrate	TON	selectivity/% C=O	selectivity/% C=C
1a	styrene	560		
1a/Hg[b]	styrene	400		
1a/NEt_3[c]	styrene	950		
1a/NEt_3/Hg[b,c]	styrene	890		
1a	benzaldehyde	650		
1a/Hg[b]	benzaldehyde	630		
1a/NEt_3[c]	benzaldehyde	20		
1a[d]	3-phenylpropionaldehyde	800		
1a	1:1 styrene−benzaldehyde[e]	600	82	18
1a/NEt_3[c]	1:1 styrene−benzaldehyde[e]	140	10	90
1a	*trans*-cinnamaldehyde	740[f]	>99	<1
1a/Hg[b]	*trans*-cinnamaldehyde	640[f]	>99	<1
1a/NEt_3[c]	*trans*-cinnamaldehyde	50[f]	46	54
1b	*trans*-cinnamaldehyde	810[f]	>99	<1
1c	*trans*-cinnamaldehyde	500[f]	98	2
2[d]	styrene	120		
2/NEt_3[c,d]	styrene	820		
2[d]	benzaldehyde	760		
2[d]	3-phenylpropionaldehyde	870		
2[d]	*trans*-cinnamaldehyde	1000[f]	>99	<1

[a] Conditions: 5.0×10^{-6} mol of precatalyst, sub:cat = 1000:1, 2 mL of toluene, 100 mg of octane (internal standard), 50 bar of H_2, 50 °C, 2 h. Conversion determined by GC. Values averaged over duplicate runs. [b] 0.1 mL of Hg. [c] 5 equiv of NEt_3. [d] Prepared under N_2. [e] Total sub:cat = 2000:1. [f] $Ph(CH_2)_3OH$ < 0.01%.

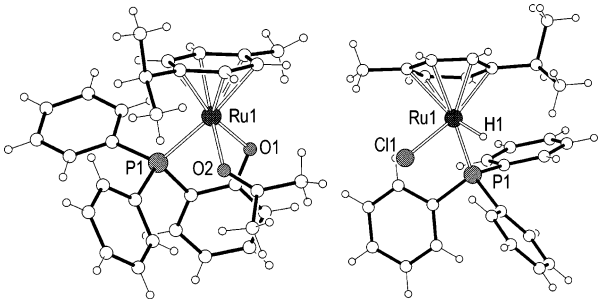
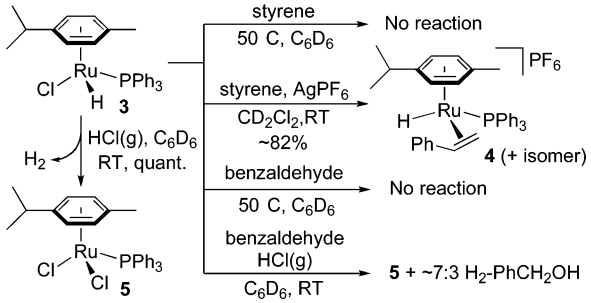


Figure 1. Ball-and-stick representations of **2** (left, counterion omitted for clarity) and **3** (right, selected molecule from asymmetric cell). Key bond lengths (Å) and angles (deg): **2**, Ru1−P1, 2.3463(9); Ru1−O1, 2.056(2); Ru1−O2, 2.126(2); Ru1−C_{av}, 2.21(3); P1−Ru1−O1, 81.89(7); P1−Ru1−O2, 82.84(6); O1−Ru1−O2, 84.07(9); **3**, Ru1−Cl1, 2.4226(6); Ru1−P1, 2.2919(7); Ru1−H1, 1.48(3); Ru1−C_{av}, 2.26(6), Cl1−Ru1−P1, 87.48(2); Cl1−Ru1−H1, 75.2(11); P1−Ru1−H1, 86.2(11).

from $[RuCl(PPh_3)_2(p\text{-cymene})]BPh_4$ using the aforementioned conditions, with PPh_3, C_6H_6, and BPh_3 as side products. The structure of **3** has been confirmed by NMR spectroscopy and X-ray diffraction (Figure 1). The hydride resonance is located at −7.44 ppm (CD_2Cl_2, 293 K, $^2J_{PH}$ = 53 Hz, T_1 = 1.75 s). Analogous C_6Me_6 and PCy_3 complexes have been reported,[10] although this appears to be the first hydride complex of this type to be characterized in the solid state by X-ray diffraction. Both at ambient temperature and at 50 °C, **3** showed no reaction with either styrene or benzaldehyde in C_6D_6 (Scheme 1). However, the olefin−hydride complex **4** (and its conformational isomer)[11,12] may be prepared in good yield (82%) from **3** by reaction with styrene and $AgPF_6$ in CD_2Cl_2. **4** and its conformational isomer are proposed to equilibrate through a 16 VE phenethyl complex via a β-hydride elimination−olefin insertion process.[11] Other precedents for this process are known for ruthenium(II)−arene complexes.[13] Addition of HCl(g) to a solution of **3** and benzaldehyde in C_6D_6 at ambient temperature resulted in the formation of $[RuCl_2(PPh_3)(p\text{-cymene})]$, **5**,[14] together with H_2 and benzyl alcohol in a ca. 7:3 ratio. Thus, HCl acts as a Lewis acid, activating the aldehyde to hydride transfer from the metal. Formation of H_2 occurs as a side product by protonation of **3** and is quantitative in the absence of benzaldehyde.

Scheme 1



Catalytic cycles for the hydrogenation of aldehydes and alkenes, depicted in Figure 2, are proposed on the basis of the above experimental observations and supported by a computational analysis (see Experimental Section). Both mechanisms involve initial phosphine dissociation, a key process identified in an earlier study,[6] and coordination of dihydrogen. An ionic outer-sphere mechanism is proposed for the hydrogenation of aldehydes,[1a,15] i.e., proton transfer to the aldehyde from a dihydrogen complex followed by hydride transfer from the resulting hydride complex (e.g., **3**). Similar ionic mechanisms have been established for the hydrogenation of imminium salts with CpRu(P−P)H (P−P = diphosphine)[16] and ketones with $[CpM(CO)_2(PR_3)(OCEt_2)]^+$ (M = Mo, W).[17] The protonation of the aldehyde is a key step in the proposed cycle, enhancing the electrophilicity of the carbonyl carbon and thus promoting hydride transfer from the metal (cf. reactions of **3** in Scheme 1); calculated Lowdin atomic charges illustrate the activation of the carbonyl carbon, whose charge increases from +0.09 in benzaldehyde to +0.21 in intermediate **D** (Figure 2).[18] This mechanism accounts for the dramatic inhibition of the catalytic activity on addition of NEt_3, which acts as a competitive base.

In the case of alkenes, heterolytic cleavage of the dihydrogen complex, **C**, and loss of HCl is suggested, leading to an olefin−hydride complex (e.g., **4**), consistent with the increased activity on addition of NEt_3.[19] β-Hydride elimination from the olefin−

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(12) The conformational isomer of **4**, **4′**, differs by the orientation of the styrene ligand; the phenyl group instead points toward the methyl group of the *p*-cymene ligand. **4** is the major isomer (**4**:**4′** = 8.2:1 (ref 11); 8.3:1 (this work)).

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(18) Additional Lowdin atomic charges (carbonyl carbon): TS_{CD}, +0.17; TS_{DB}, +0.18; benzyl alcohol, −0.04.

(19) Consistent with the base poisoning experiments, using the more basic solvent THF, instead of toluene, higher activities for the hydrogenation of styrene are observed under equivalent conditions using **1a** also (see ref 6).

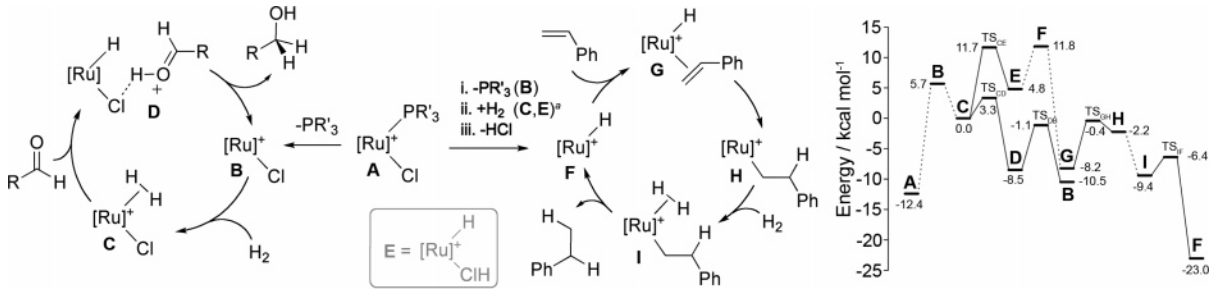

Figure 2. Proposed catalytic cycles for the hydrogenation of aldehydes (left) and alkenes (center) with calculated energies (right). Calculations were carried out using a model system, where [Ru] = $Ru(PPh_3)(C_6H_6)$ and R = R′ = Ph. [a]**E** is a (computed) intermediate in the heterolytic cleavage of dihydrogen in **C**.

hydride complex followed by dihydrogen coordination and σ-bond metathesis close the catalytic cycle. A related mechanism has been established for $RuCl_2(PPh_3)_3$, whose catalytic activity is similarly increased by addition of bases such as NEt_3, which promote heterolytic cleavage of dihydrogen, leading to the active catalyst $RuHCl(PPh_3)_3$.[1,20] This pathway should be less significant for the chelating complex **2**, and correspondingly lower activity is observed for the hydrogenation of styrene (without NEt_3). Furthermore, the calculated energy barrier for the heterolytic cleavage in the alkene cycle (**C** → **E**) is 3.5 times larger than proton transfer to the aldehyde (**C** → **D**), in line with the observed selectivity.

To conclude, bis-phosphine ruthenium(II)−arene complexes exhibit both high activity and chemoselectivity for the catalytic hydrogenation of aldehydes. From the evidence presented herein an ionic outer-sphere mechanism is proposed for this process.

Experimental Section

General Methods. All organometallic manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a dry-nitrogen glovebox. CH_2Cl_2, toluene, pentane, diethyl ether, and THF were dried catalytically under nitrogen using a solvent purification system, manufactured by Innovative Technology Inc. Octane and acetone were distilled from CaH_2 and $CaSO_4$, respectively, and stored over molecular sieves under nitrogen. CD_2Cl_2 and C_6D_6 were distilled from CaH_2 and K, respectively, and stored under nitrogen. All other solvents were p.a. quality and saturated with nitrogen prior to use. $[RuCl(PPh_3)(P(p\text{-tol})_3)(p\text{-cymene})]PF_6$,[6] $[RuCl(PPh_3)_2(p\text{-cymene})]PF_6$,[6] $[RuCl(P(p\text{-tol})_3)_2(p\text{-cymene})]PF_6$,[6] $[RuCl\text{-}(\kappa^2\text{-}PPh_2C_6H_4O)(p\text{-cymene})]$,[6] and $[RuCl_2(PPh_3)(p\text{-cymene})]$[14] were prepared as described elsewhere. Styrene, benzaldehyde, 3-phenylpropionaldehyde, and *trans*-cinnamaldehyde were saturated with nitrogen and stored over molecular sieves. All other chemicals are commercial products and were used as received. NMR spectra were recorded on a Bruker Avance 400 spectrometer at room temperature (293 K), unless otherwise stated (see Supporting Information for NMR labelling schemes). The T_1 relaxation measurement was preformed at 400 MHz by the standard inversion−recovery method. High-pressure in situ NMR measurements were performed in sapphire NMR tubes.[21] Chemical shifts are given in ppm and coupling constants (J) in Hz. Microanalyses were performed at the EPFL.

Preparation of $[Ru(\kappa^2\text{-}PPh_2C_6H_4O)(OCMe_2)(p\text{-cymene})]PF_6$ (2). A suspension of $[RuCl(\kappa^2\text{-}PPh_2C_6H_4O)(p\text{-cymene})]$ (0.238 g, 0.43 mmol) and $AgPF_6$ (0.121 g, 0.48 mmol) in a mixture of CH_2Cl_2−acetone (5:1 v/v, 18 mL) was stirred in the dark at RT for 1 h. The solution was then filtered through dry Celite, washing with CH_2Cl_2 (4 × 5 mL). Acetone (20 mL) was then added to the filtrate, which was then concentrated to ca. 10 mL. Addition of pentane (50 mL) gave the product as a microcrystalline orange solid, which was filtered, washed with pentane (3 × 10 mL), and dried under a stream of nitrogen. Yield: 0.27 g (86%). Crystals suitable for X-ray diffraction were grown by layering a CH_2Cl_2−acetone (∼1:1 v/v) solution of the complex with pentane. ^1H NMR (CD_2Cl_2): δ 7.45−7.79 (m, 10H, PPh_2), 7.20−7.28 (m, 1H, H^{14}), 7.13−7.20 (m, 1H, H^{12}), 6.93−6.99 (m, 1H, H^{15}), 6.64−6.71 (m, 1H, H^{13}), 5.96 (br, 1H, H^3), 5.75 (br, 1H, H^6), 5.34 (br, 1H, H^2), 4.97 (br, 1H, H^5), 2.60 (sept, $^3J_{HH}$ = 6.9, 1H, H^8), 2.16 (s, 6H, H^{18}), 2.11 (s, 3H, H^7), 1.28 (broad d, $^3J_{HH} \approx 7$, 3H, H^9), 1.10 (br d, $^3J_{HH} \sim 7$, 3H, H^{10}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 229 (C^{17}), 177.6 (d, $^2J_{PC}$ = 20, C^{16}), 127−135 (m, PPh_2), 133.5 (s, C^{14}), 132.7 (s, C^{12}), 119.1 (d, J_{PC} = 9, C^{15}), 116.6 (d, $^3J_{PC}$ = 8, C^{13}), 112.4 (d, $^1J_{PC}$ = 56, C^{11}), 106.0 (br, C^4), 97.6 (s, C^1), 88.7 (br, C^3), 88 ($C^2 + C^6$), 81.4 (br, C^5), 31 ($C^8 + C^{18}$), 22.3 (br, C^9), 21.2 (br, C^{10}), 17.7 (s, C^7). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 56.2 (s, 1P, $RuPPh_3$), −144.3 (sept, $^1J_{PF}$ = 711, 1P, PF_6). $^{31}P\{^1H\}$ NMR ($OC(CD_3)_2$): δ 55.7 (s, 1P, $RuPPh_3$), −144.1 (sept, $^1J_{PF}$ = 708, 1P, PF_6). Anal. Calcd for $C_{31}H_{34}F_6O_2P_2Ru$ (715.62 g mol^{-1}): C, 52.03; H, 4.79. Found: C, 52.07; H, 4.65.

Preparation of $[RuCl(PPh_3)_2(p\text{-cymene})]BPh_4$. A suspension of $[RuCl_2(PPh_3)(p\text{-cymene})]$ (0.300 g, 0.53 mmol), PPh_3 (0.277 g, 1.06 mmol), and $NaBPh_4$ (0.22 g, 0.64 mmol) in MeOH (30 mL) was stirred at 35 °C for 2 h. The resulting precipitate was then isolated by filtration, washed with EtOH (2 × 15 mL), and extracted with CH_2Cl_2 (60 mL) through Celite. Addition of MeOH (50 mL) and slow concentration gave the product as a microcrystalline orange solid. Yield: 0.51 g (86%). NMR data were in agreement with analogous compounds;[6,22] selected data are included for reference. ^1H NMR ($CDCl_3$): δ 6.74−7.48 (m, 50H, *Ph*), 5.06−5.12 (m, 2H, H^2), 4.82 (d, $^3J_{HH}$ = 6.2, 1H, H^3), 2.67 (sept, $^3J_{HH}$ = 6.9, 1H, H^8), 1.23 (d, $^3J_{HH}$ = 7.0, 6H, H^7), 0.50 (s, 3H, H^5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.8 (s, $RuPPh_3$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 86.7 (s, BPh_4). Anal. Calcd for $C_{70}H_{64}BClF_6P_2Ru$ (1114.56 g mol^{-1}): C, 75.44; H, 5.79. Found: C, 75.62; H, 5.76.

Preparation of $[RuHCl(PPh_3)(p\text{-cymene})]$ (3). In a glovebox, a 300 mL capacity autoclave, containing a Teflon liner and glass vessel, was charged with $[RuCl(PPh_3)_2(p\text{-cymene})]BPh_4$ (0.70 g, 0.22 mmol), THF (30 mL), and a magnetic stirrer bar. The autoclave was removed from the glovebox, flushed with H_2 (3 × 15 bar), and pressurized with H_2 (50 bar). The system was heated at 50 °C for 90 min and cooled and the pressure partially released (to ca. 5 bar) before being placed back into the glovebox. The remaining pressure was released, the solution transferred into a round-bottom flask, and the solvent removed in vacuo. The residue was then extracted with diethyl ether (20 mL) and the filtered solution reduced to dryness. The residue was then suspended in a mixture of pentane (50 mL) and diethyl ether (2 mL), stirred briefly, filtered, and washed with pentane (20 mL) to afford the product as a bright

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yellow, air-sensitive powder. Yield: 0.23 g (66%). Crystals suitable for X-ray diffraction were grown by layering a diethyl ether solution of the complex with pentane in a glovebox. ^{1}H NMR (CD_2Cl_2): δ 7.30−7.77 (m, 15H, P*Ph*$_3$), 5.68 (2, $^3J_{HH}$ = 6.2, 1H, H^3), 5.12 (d, $^3J_{HH}$ = 5.5, 1H, H^6), 4.89 (d, $^3J_{HH}$ = 6.1, 1H, H^2), 4.10 (d, $^3J_{HH}$ = 5.5, 1H, H^5), 2.17 (sept, $^3J_{HH}$ = 6.9, 1H, H^8), 2.03 (s, 3H, H^7), 1.26 (d, $^3J_{HH}$ = 6.8, 3H, H^9), 1.15 (d, $^3J_{HH}$ = 6.8, 3H, H^{10}), −7.44 (d, $^2J_{PH}$ = 53, 1H, Ru-*H*, T^-_1 = 1.75 s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 136.8 (d, $^1J_{PC}$ = 46, P*Ph*$_3$), 133.8 (d, $^2J_{PC}$ = 11, P*Ph*$_3$), 129.6 (d, $^4J_{PC}$ = 2, P*Ph*$_3$), 127.8 (d, $^3J_{PC}$ = 10, P*Ph*$_3$), 109.3 (d, $^2J_{PC}$ =,^{2} C^4), 104.0 (s, C^1), 91.9 (d, $^2J_{PC}$ = 5, C^2), 89.4 (d, $^2J_{PC}$ = 2, C^6), 87.3 (d, $^2J_{PC}$ = 7, C^3), 80.1 (d, $^2J_{PC}$ = 1, C^5), 31.2 (s, C^8), 24.0 (s, C^{10}), 22.6 (s, C^9), 18.5 (s, C^7). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 52.5 (s, Ru*P*Ph$_3$). ^{31}P NMR (CD_2Cl_2): δ 52.5 (d, $^2J_{PH}$ = 54, Ru*P*Ph$_3$). Anal. Calcd for $C_{28}H_{30}ClPRu$ (534.04 g mol^{-1}): C, 62.97; H, 5.66. Found: C, 63.03; H, 5.67.

Reactions of [RuHCl(PPh$_3$)(η^6-*p*-cymene)] (3). Reactions of **3** were carried out in a screw-cap NMR tube, with the samples prepared in a glovebox. Yields were calculated from integration of NMR spectroscopic data. (a) Attempted reaction with styrene: A solution of **3** (4 mg) and styrene (1 μL, 1.2 equiv) in C_6D_6 (0.5 mL) was heated at 50 °C for 15 min. (b) Reaction with styrene and $AgPF_6$: A suspension of **3** (7.0 mg), styrene (2 μL, 1.3 equiv), and $AgPF_6$ (5.3 mg, 1.6 equiv) in CD_2Cl_2 (0.5 mL) was stirred in the absence of light at RT for 20 min and then filtered through Celite into a screw-cap NMR tube and analyzed by NMR spectroscopy. (c) Reaction with benzaldehyde: A solution of **3** (10.0 mg) and benzaldehyde (2 μL, 1.1 equiv) in C_6D_6 (0.5 mL) was heated at 50 °C for 15 min. No reaction was observed by NMR spectroscopy. HCl(g) (10 mL, excess) was bubbled through the cooled solution, resulting in the solution turning red instantly. The solution contained [$RuCl_2$(PPh_3)(*p*-cymene)] (**5**, verified further by ^{31}P{^{1}H} NMR), H_2, $PhCH_2OH$ (**5**:$PhCH_2OH$ ≈ 7:3), and PhCHO as identified by ^{1}H NMR spectroscopy. Bubbling N_2 through the solution removed the peak corresponding to H_2. (d) Reaction with HCl(g): HCl(g) (10 mL, excess) was bubbled through a solution of **3** (5.0 mg) in C_6D_6 (0.5 mL), which turned red immediately.

Catalytic Procedures. All catalytic experiments were conducted using a home-built multicell autoclave containing an internal temperature probe. Each glass reaction vessel was charged with the precatalyst (5.0×10^{-6} mol), substrate (0.005 mol, S:C = 1000: 1), internal standard (100 mg of octane), and solvent (2 mL of toluene) and then placed inside the autoclave and sealed. This procedure was carried out either in air (general procedure for **1**) or in a glovebox (for **2**). Following flushing with H_2 (3 × 10 bar), the autoclave was heated to 50 °C under H_2 (5 bar, ca. 10 min) and then maintained at 50 bar for the duration of the catalytic run (2 h). The autoclave was then cooled to ambient temperature (<5 min) using an external water-cooling system, and then the pressure was released. Conversions were determined by GC analysis of the samples using a Varian chrompack CP-3380 gas chromatograph, with species verified by comparison to authentic samples.

Computational Methods. All geometry optimizations and frequency calculations were carried out using the Gaussian03 suite of programs.[23] Geometries were optimized and verified by harmonic analysis using the ONIOM approach,[24] with the phenyl groups constituting the low layer; all other atoms where included in the high layer. The model chemistry of the low layer was HF, and the LanL2MB basis set was used for all atoms; LanL2MB pseudopotentials were used for Ru, P, and Cl. B3LYP was used for the high layer, with the 6-31G(d,p) basis set used for all atoms except Ru, for which the LanL2DZ basis set was used; LanL2DZ pseudopotentials were used for Ru, P, and Cl. Energies were calculated by single-point SCF calculation on the full optimized geometry at the B3LYP level using the high-layer basis sets, with the LanL2DZ pseudopotential for Ru, and are not zero-point-corrected. A pruned grid consisting of 75 radial shells and 302 angular points was used for all calculations. Energies for the small molecules used in this study are compiled in Table S1, with the optimized geometries and energies of **A**−**F** listed in Table S2.

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Supporting Information Available: Crystallographic details, X-ray data and tables; optimized geometries and energies; NMR labelling schemes and spectra of **3**; crystallographic information for **2** and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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