Homogeneous Catalysis

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Ruthenium(II) Terdentate CNN Complexes: Superlative Catalysts for the Hydrogen-Transfer Reduction of Ketones by Reversible Insertion of a Carbonyl Group into the Ru–H Bond**

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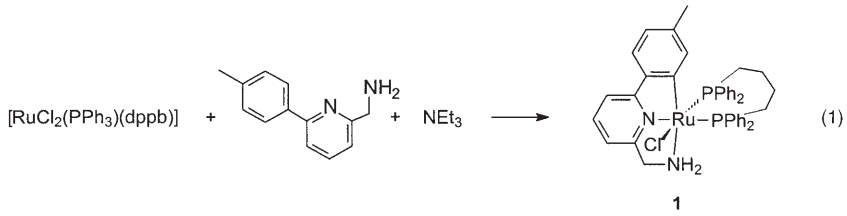
Dedicated to Professor Fausto Calderazzo on the occasion of his 75th birthday

Pincer ECE (E = N, P) transition-metal complexes, in which the terdentate ligands contain two stable five-membered cyclometalated rings, have reached a high level of sophistication and appear extremely attractive for both catalytic and stoichiometric reactions.[1] The great interest in pincer ligands arises from the high level of control over the reactivity and the stereochemistry that they impose around the metal center as a result of their electronic properties and geometric restrictions. These factors afford highly selective transformations and lead to some unique species of relevance for the investigation of elementary processes.[2] In spite of the great attention afforded to ruthenium for its versatility in catalysis,[3] no examples of terdentate ruthenium CNN catalysts have been reported thus far. It is worth noting that CNN complexes are expected to have significantly different reactivity compared to the NCN analogues, mainly because of the different geometrical disposition of the σ-donor carbon atom.

Recently, we have shown that 2-(aminomethyl)pyridine (ampy) shows a high ligand acceleration effect in transfer hydrogenation[4] catalyzed by ruthenium(II) complexes with phosphane ligands. Thus, complete reduction of many ketones in 2-propanol is quickly achieved with the cyclometalated complex [RuCl(CO)(CP)(ampy)] (CP = (2-CH_2-6-MeC_6H_3)PPh_2), with turnover frequencies (TOF values) up to $6.3\times10^4\ h^{-1}$, whereas the derivatives *cis*-[$RuCl_2$(PP)(ampy)] (PP = diphosphane) lead to TOF values up to $4.0\times10^5\ h^{-1}$ and *ee* values up to 94% by using chiral diphosphanes.[5] Since it is well known that 2-phenylpyridine readily gives access to orthometalated CN ruthenium complexes,[6] we decided to investigate the coordination chemistry of the related 6-(4′-methylphenyl)-2-pyridylmethylamine with the aim of obtaining terdentate CNN complexes. We report herein on novel complexes of formula [RuX(CNN)(dppb)] (X = Cl, H; dppb = $Ph_2P(CH_2)_4PPh_2$), which are remarkably active catalysts for transfer hydrogenation that afford TOF values up to $2.5\times10^6\ h^{-1}$ with very low loading of catalysts (0.005–0.001 mol%) compared to the most active systems reported.[2f,7] Evidence is provided that the reduction of the ketone proceeds through the formation of a Ru^{II}–alkoxide complex by insertion of the carbonyl group of the substrate into the Ru–H bond of a ruthenium(II) hydride formed as an intermediate from the chloride complex **1**.

Treatment of [$RuCl_2(PPh_3)$(dppb)] with an equimolar amount of 6-(4′-methylphenyl)-2-pyridylmethylamine in 2-propanol at reflux in the presence of NEt_3 affords the thermally stable orthometalated ruthenium(II) complex **1**[8] in high yield [Eq. (1)].



1 (1)

The signals for the diastereotopic NCH_2 protons in the ^{1}H NMR spectrum are at $\delta = 4.12$ and 3.72 ppm with $^2J(H,H) = 15.5$ Hz. The doublet at $\delta = 52.5$ ppm with a $^3J(C,P) = 2.7$ Hz in the ^{13}C NMR spectrum corresponds to the CH_2N group which is shifted downfield relative to the free ligand ($\delta = 48.2$ ppm), thus indicating coordination of the NH_2 group to the metal center. Finally, the signal for the orthometalated carbon atom appears as a doublet of doublets at $\delta = 181.8$ ppm with $^2J(C,P) = 16.3$ and 7.8 Hz, which is strongly shifted downfield[6a,9] relative to the free ligand ($\Delta\delta = 54.8$), thus allowing the former formulation to be established unambiguously in solution. The X-ray analysis carried out on a single crystal of **1** shows a severely distorted octahedral environment around the ruthenium center comprising the orthometalated terdentate pyridine ligand, the diphosphane, and a chloride ligand (Figure 1).[10]

The two N1-Ru-C1 and N1-Ru-N2 bond angles in the five-membered rings are rather small, (80.32(13) and 76.45(12)°, respectively) because of the geometrical constrains of the terdentate ligand. The Ru–N2 bond length of 2.246(3) Å is significantly longer than the Ru–N1 bond (2.046(3) Å) because of the *trans* influence exerted by the aryl group. The terdentate ligand presents coplanar atoms with the exception of the CH_2NH_2 group, the carbon and amino nitrogen atoms of which are displaced by −0.13 and 0.53 Å,

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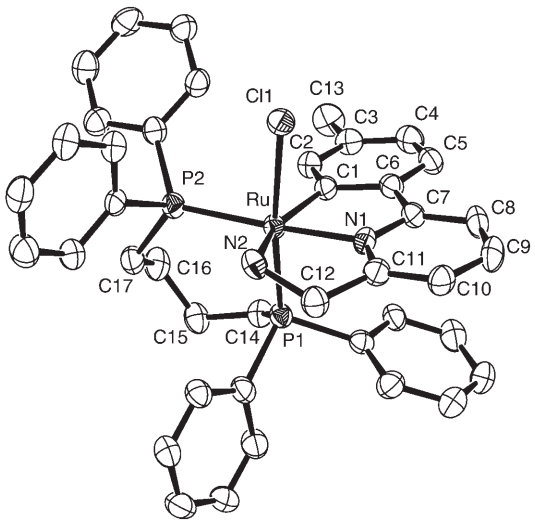
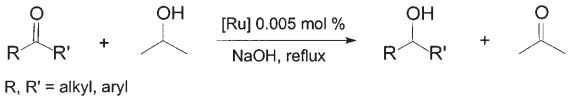


Figure 1. ORTEP representation of complex **1**. Thermal ellipsoids are at 40% probability, the labeling scheme of the phenyl carbon atoms is omitted for clarity. Selected coordination bond lengths [Å] and angles [°]: Ru-C1 2.057(4), Ru-N1 2.046(3), Ru-N2 2.246(3), Ru-P1 2.252(1), Ru-P2 2.287(1), Ru-Cl1 2.495(1); N1-Ru-C1 80.32(13), N1-Ru-N2 76.45(12), N2-Ru-P1 102.59(8), N1-Ru-P2 173.00(8), C1-Ru-P2 103.60(10), N2-Ru-P2 98.74(8), P1-Ru-P2 94.85(4), P1-Ru-Cl1 173.29(3), C1-Ru-N2 155.40(12), C1-Ru-P1 85.78(9), N1-Ru-P1 91.20(8).

respectively, from the mean plane. Related terdentate Pt^{II} and Pd^{II} complexes obtained from 6-phenyl-2-(2-aminoisopropyl)pyridine have recently been reported.[11]

Complex **1** has been found to display an exceptionally high catalytic activity in the reduction of a large number of ketones (0.1M) with 2-propanol as the hydrogen donor and in the presence of NaOH (2 mol%) [Eq. (2)].



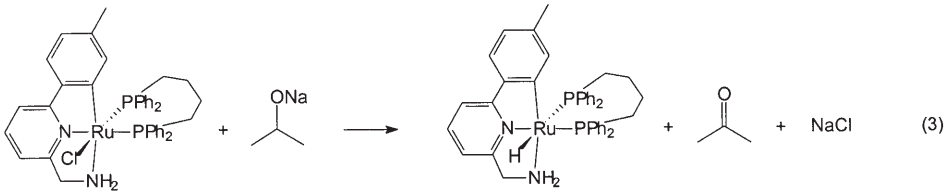
(2)

R, R' = alkyl, aryl

Acetophenone is quantitatively reduced to 1-phenylethanol in five minutes using a substrate/**1** ratio of 20000:1 with a remarkably high TOF value of $1.1\times10^6\ h^{-1}$ at 50% conversion (Table 1). Subsequent addition of further amounts of the ketone (two times) results in complete reduction, thus suggesting that the stability of the complex results from the rigid framework built up by the association of the robust terdentate ligand with the chelating diphosphane, and consequently catalyst deactivation is significantly retarded.

Complex **1** can also be generated in situ from [$RuCl_2$-(PPh_3)(dppb)] and the functionalized pyridine ligand (1:2 molar ratio) in 2-propanol and it shows the same activity as the isolated compound. In contrast, the in situ prepared analogue of **1** bearing $N(CH_3)_2$ instead of the NH_2 group shows low activity for acetophenone (Ru 0.005 mol%, NaOH 2 mol%, 7% conversion after 1 h) under identical experimental conditions, thus suggesting that the high performance of **1** is in someway related to an assistance of the NH group in the catalytic cycle. Interestingly, complete reduction (98%) is achieved in 1 h with a substrate/**1** ratio of 100000:1 (TOF = $5.2\times10^5\ h^{-1}$), and experiments at lower catalyst loading (0.0005 mol%) led to a turnover number (TON) of 1.7×10^5. These results are of particular relevance for large-scale synthesis since hydrogen-transfer catalysts are usually used in the range of 1–0.01 mol% as a consequence of their easy deactivation, with TOF values lower than $10^5\ h^{-1}$. As shown in Table 1, alkyl–aryl, dialkyl (cyclic and linear), and diaryl ketones are rapidly (minutes), quantitatively, and chemoselectively reduced to alcohols with TOF values in the range 5.0×10^5 to $2.5\times10^6\ h^{-1}$ with 0.005 mol% of **1**. The high performance of **1** means that this protocol allows the preparation of alcohols on a gram scale using very low amounts of catalyst.[12]

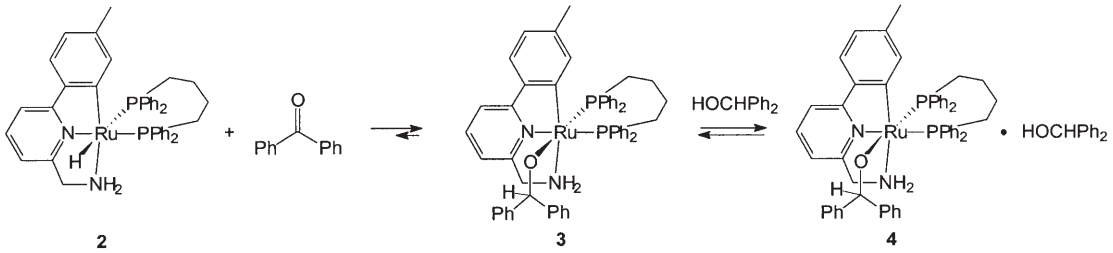
It is generally accepted that the role of the base in ruthenium-catalyzed hydrogen-transfer reactions is to generate hydrides, which are the catalytic active species.[13] In agreement with this, we have found that reaction of **1** with sodium isopropoxide in a 2-propanol/toluene solution affords the orange hydride complex **2**[14] through elimination of acetone on evaporation of the medium [Eq. (3)].



1 **2** (3)

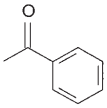
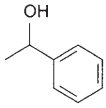
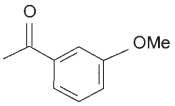
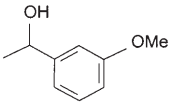
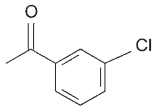
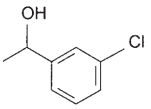
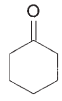
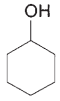
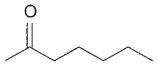
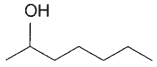
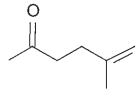
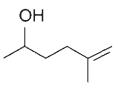
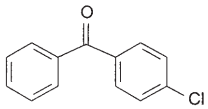
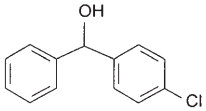
The ^{31}P NMR spectrum of **2** displays two doublets at δ = 65.7 and 34.6 ppm with a relatively small $^2J(P,P)$ coupling constant of 17.2 Hz. The resonance of the hydride in the ^1H NMR spectrum appears as a doublet of doublets at δ = −5.58 ppm with $^2J(H,P) = 89.1$ and 26.4 Hz, which is consistent with the presence of *trans* and *cis* phosphorus atoms.[15] An IR band of medium intensity appears at $\tilde{\nu} = 1743\ cm^{-1}$ corresponding to the Ru–H species and this low-frequency shift is in agreement with the strong *trans* influence of the phosphane ligand.[16] It is noteworthy that addition of hydride **2** (1 mol%) to acetophenone and 2-propanol (1:1 molar ratio) in C_6D_6 leads, at room temperature and within a few minutes, to an equilibrium mixture in which 1-phenylethanol and acetone are formed. Hydride **2** is a catalyst of impressive activity in 2-propanol at reflux which leads to complete conversion of acetophenone in a few minutes with TOF values ranging from $4.8\times10^4\ h^{-1}$ (**2** 0.01 mol%, in the absence of any additional base) to $8.0\times10^5\ h^{-1}$ (in the presence of a tenfold excess of NaO*i*Pr).

Complex **2** reacts promptly with an equimolar amount of benzophenone in C_6D_6 at 20°C to give the alkoxide–amine complex **3**[17] through insertion of the ketone into the Ru–H bond (Scheme 1).



Scheme 1.

Table 1: Catalytic reduction of ketones (0.1 M) with **1** (0.005 mol%) and NaOH (2 mol%) in 2-propanol at 82 °C.

Ketone	Alcohol	Conversion [%][a]	min	TOF [h^{-1}][b]
		98	5	1.1×10^6
		98	2	1.9×10^6
		99	1	2.5×10^6
		99	5	1.2×10^6
		97	2	1.5×10^6
		99	10	5.0×10^5
		97	5	7.0×10^5
		98	10	5.3×10^5

[a] The conversion was determined by GC or ^{1}H NMR analysis. [b] Turnover frequency (mol of ketone converted into alcohol per mol of catalyst per hour) at 50% conversion.

The ^{31}P NMR spectrum of **3** shows two doublets at $\delta =$ 57.0 and 37.3 ppm with $^2J(P,P) = 34.2$ Hz; this coupling constant is slightly smaller than that of **1** ($^2J(P,P) = 38.3$ Hz). The proton signal for the RuOCH moiety appears as a doublet at $\delta = 4.80$ ppm (0 °C in [D_8]toluene) with $^4J(H,P) =$ 3.7 Hz, whereas one broad resonance shifted downfield to $\delta =$ 5.30 ppm arises from one proton of the amine group, which may suggest an NH···O hydrogen bond interaction that stabilizes the alkoxide **3**. The ^{13}C NMR peak of the OCH moiety in C_6D_6 appears at $\delta = 80.1$ ppm and it is shifted downfield relative to free benzhydrol ($\delta = 76.1$ ppm), a result which is in agreement with other metal alkoxides.[18] NMR spectroscopic studies show that heating a solution of **3** in [D_8]toluene above 70 °C results in reversible generation of both the ketone and the hydride **2**.

The alkoxide **3** is sensitive to protic compounds and the corresponding alcohol adducts are observed in the presence of alcohols.[19] Addition of benzhydrol (2 equivalents) to **3** results in the formation of the species **4** (^{31}P NMR: $\delta = 55.0$ and 42.8 ppm, with $^2J(P,P) = 34.2$ Hz), according to the equilibrium shown in Scheme 1 (**3**/**4** ca. 1.5:1). Heating the solution results in an increase of **3**, and coalescence of the signals for **3** and **4** is observed at about 60 °C. Elimination of benzhydrol has been observed with more acidic compounds such as water or carboxylic acids.[20] It is worth noting that a ^{31}P NMR spectroscopic study of the reaction of **1** with Na*i*OPr in 2-propanol/toluene to give the hydride **2** shows two doublets at $\delta = 54.3$ and 44.6 ppm, with $^2J(P,P) = 34.2$ Hz. These values are close to those of **4**, thus suggesting the formation of a similar adduct between the ruthenium isopropoxide and 2-propanol. A variable temperature NMR study shows that heating this solution above 40 °C leads to an equilibrium reaction between the Ru-isopropoxide and the hydride **2**, whose concentration can also be increased by elimination of acetone through evaporation (in agreement with the reaction of benzophenone shown in Scheme 1).

While the insertion of unsaturated compounds into the Ru–H bond has been thoroughly studied, examples of the formation of Ru–alkoxides by reaction of ketones are rare and restricted to ketoesters or to substrates containing an additional electron-withdrawing group.[21] The reverse reaction, that is, β-hydrogen elimination,[22] provides one of the

most practical routes to metal hydrides. The reversibility of this process, however, has been clearly established only for $[Re_3(\mu\text{-}OiPr)_3(OiPr)_6]$,[23a] although spectroscopic evidence has been collected at low temperature for $[OsCl(OCH(CD_3)_2)(CO)(PiPr_3)_2]$.[23b] Recently, the NH-assisted reversible insertion of CO_2 into the Ru–H bond to give the formate–amine species has been reported by Koike and Ikariya.[24] Interestingly, spectroscopic evidence of ruthenium–alkoxide–amine species has been obtained starting from ruthenium–amide complexes and alcohols.[25]

The results of the study on the stoichiometric reactions of the CNN complexes, together with the influence of the alkoxide concentration on the catalytic activity of the hydride **2**, provide strong support to the formation of a discrete intermediate Ru–alkoxide species in the course of the catalytic transfer hydrogenation of ketones. As this fact cannot be explained by the concerted outer-sphere mechanism first proposed by Noyori and co-workers for ruthenium catalysts containing ligands with NH donor groups (metal–ligand bifunctional catalysis),[4b,26] an alternative mechanism for this process may be envisioned as follows. The catalytically active Ru–isopropoxide species, which is formed from **1** and sodium isopropoxide, equilibrates with hydride **2**. Insertion of the ketone into the Ru–H bond of **2** provides a new ruthenium alkoxide, such as **3**. The latter, on exchange with 2-propanol, delivers the reaction product and regenerates the Ru–isopropoxide complex, thus closing the catalytic cycle. Although the classical ketone insertion into the metal-hydride bond and the β-hydrogen elimination pathways,[4e,27] involving a *cis* vacant site (that is, through dissociation of the NH_2 moiety), cannot be ruled out, it is more likely that both elementary steps occur through hydrogen-bond assistance of the NH_2 group, without NH proton transfer. For example, the development of an NH···O=C interaction between the amine and the incoming ketone may at the same time activate the substrate towards the nucleophilic attack and provide the ketone with the correct orientation for the hydride transfer to be feasible. The resulting alkoxide anion might then migrate from the hydrogen to the metal center, possibly through a three-centered reaction mechanism, to afford the Ru–alkoxide intermediate. Thus, the formation of the Ru hydride from the Ru alkoxide may occur through the reverse pathway. Strong hydrogen bonding between the substrate, catalyst, and solvent probably plays a key role in the overall process. Theoretical studies on the mechanism of the transfer hydrogenation with Ru/NH catalysts show that ruthenium methoxide–amine complexes are the most stable species along the reaction pathways.[26b,28]

Finally, it is worth noting that our approach can be easily extended to the high-speed enantioselective transfer hydrogenation. Thus, when $[RuCl_2(PPh_3)(dppb)]$ is treated with the chiral derivative of 6-phenyl-2-pyridylmethylamine with a *t*Bu group on the $CHNH_2$ arm (*R* enantiomer), rapid conversion of *o*-methoxyacetophenone into (*S*)-*o*-methoxy-α-phenylethanol is observed (Ru 0.05 mol%, $TOF = 6.0 \times 10^5\ h^{-1}$, $ee = 87\%$), in agreement with the non-hemilabile behavior of the NH_2 function of the CNN ligand.

In summary, we have shown that terdentate [RuX(CNN)(PP)] (X = Cl, H) complexes are highly efficient catalysts in transfer hydrogenation involving 2-propanol to afford quantitative reduction of different ketones with very low loading and in a short time. Reduction of ketones apparently takes place by insertion of the substrate into the Ru–H bond, thus leading to a Ru^{II} alkoxide. The reversibility of this step has been observed in the case of the stoichiometric reaction of complex **2** with benzophenone. This fact provides strong evidence that a Ru alkoxide derivative is most probably an intermediate in the formation of the hydride **2**, the putative active catalyst, from the relevant chloride **1**. As the structure of the terdentate pyridine ligand is well suited for a modular synthetic approach, which allows for a fine tuning of the stereoelectronic properties of the CNN complexes, this new class of ruthenium derivatives holds the promise for a broad application in organometallic chemistry and in homogeneous asymmetric catalysis.

Experimental Section

1: $[RuCl_2(PPh_3)(dppb)]$ (1.17 g, 1.36 mmol) was added to a solution of 2-propanol (15 mL) containing 6-(4′-methylphenyl)-2-pyridylmethylamine (300 mg, 1.51 mmol) and NEt_3 (1.9 mL, 13.6 mmol). The mixture was refluxed for 2 h and the yellow precipitate was filtered, washed with methanol, and dried under reduced pressure. Yield: 810 mg (78%).

2: Compound **1** (516 mg, 0.679 mmol) was suspended in toluene (10 mL) and a solution of NaO*i*Pr (0.1M, 1.00 mmol) in 2-propanol (10 mL) was added. The solution was concentrated after 1 h at 60°C, stirred at room temperature, and after addition of toluene, filtered over celite. The filtrate was evaporated and the solid was precipitate from toluene and filtered, to afford a bright orange product which was dried under reduced pressure. Yield: 395 mg (80%).

3: Benzophenone (45 mg, 0.247 mmol) was added to a suspension of **2** (160 mg, 0.220 mmol) in toluene (2 mL), and the solution was stirred for 15 min. The solution was then concentrated and pentane added. This afforded a dark yellow precipitate which was filtered and dried under reduced pressure. Yield: 140 mg (70%).

Typical procedure for the catalytic hydrogen-transfer reaction: Complex **1** (3.0 mg, 4.0 μmol) was dissolved in 2-propanol (8 mL). The ketone (2 mmol) was dissolved in 2-propanol (19 mL) and the solution heated to reflux under argon. Addition of NaOH (0.1M, 400 μL) and the solution containing the catalyst **1** (200 μL) resulted in the reduction of the ketone starting immediately. The yield was determined by GC or NMR analysis (ketone:**1**:NaOH = 20000:1:400; ketone 0.1M).

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Keywords: homogeneous catalysis · hydride · hydrogenation · orthometalation · ruthenium

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[8] **1**: ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C, TMS): $\delta = 8.10$–6.57 (m, 24H; ArH), 6.00 (t, J(H,H) = 8.1 Hz, 2H; *m*-Ph), 4.12 (dd, J(H,H) = 15.5, 4.4 Hz, 1H; CH_2N), 3.72 (td, J(H,H) = 15.5, 4.1 Hz, 1H; CH_2N), 3.41 (m, 1H; NH_2), 3.05 (m, 2H; CH_2P), 2.46–0.90 (m, 7H; NH and CH_2), 2.23 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, 20 °C, TMS): $\delta = 181.8$ (dd, J(C,P) = 16.3, 7.8 Hz; CRu), 163.2 (s; N*C*C), 155.9 (s; N*C*CH_2), 149.2–116.0 (m; Ar), 52.5 (d, J(C,P) = 2.7 Hz; CH_2N), 33.4 (d, J(C,P) = 26.3 Hz; *C*H_2P), 30.7 (d, J(C,P) = 31.6 Hz; CH_2P), 26.8 (s; CH_2), 22.1 (s; CH_2), 21.8 ppm (s, CH_3); ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 20 °C, H_3PO_4): $\delta = 57.3$ (d, J(P,P) = 38.3 Hz), 42.6 ppm (d, J(P,P) = 38.3 Hz); elemental analysis (%) calcd for $C_{41}H_{41}N_2ClP_2Ru$: C 64.77, H 5.44, N 3.68; found: C 64.36, H 5.52, N 3.70.

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[10] Crystal structure analysis of **1**·2 C_6H_6, $C_{53}H_{53}N_2ClP_2Ru$, M_r = 916.43, triclinic, space group $P\bar{1}$, $a = 11.547(3)$, $b = 13.307(3)$, $c = 16.400(4)$ Å, $\alpha = 84.38(3)$, $\beta = 74.29(3)$, $\gamma = 69.38(2)$°, V = 2270.4(10) Å^3, $Z = 2$, $\rho_{calcd} = 1.341$ g cm^{-3}, $\mu = 4.285$ mm^{-1}, F-(000) = 952, $\theta = 3.55$–64.82°. Final $R_1 = 0.0487$, $wR_2 = 0.1262$, $S = 1.087$ for 533 parameters and 6542 reflections (of which 6251 with $I > 2\sigma(I)$), max positive and negative peaks in ΔF map 0.547 and -0.689 e Å^{-3}. Data were collected at 160(2) K on a Nonius FR590 rotating anode ($Cu_{K\alpha}$ radiation, $\lambda = 1.54178$ Å) equipped with KappaCCD detector. CCDC-265691 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[12] For example, 1.97 g of the pharmaceutical intermediate 4-chlorobenzhydrol (90% yield) was obtained from 4-chlorobenzophenone in 2-propanol (NaOH 2 mol%) after 2 h at reflux and using **1** (0.076 mg from a standard solution) (ketone/catalyst = 100000:1).

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[17] **3**: ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C, TMS): $\delta = 8.40$–5.80 (m, 35H; ArH), 5.58 (d, J(H,H) = 7.2 Hz, 1H; ArH), 5.35 (brs, 1H; NH_2), 4.86 (s, 1H; OCH), 3.20–2.60 (m, 5H), 2.25 (s, 3H; CH_3), 2.10–0.9 ppm (m, 6H); ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 20 °C, TMS): $\delta = 187.6$ (s; CRu), 163.8 (s; N*C*C), 157.4 (s; N*C*CH_2), 155.7–112.4 (m; Ar), 80.1 (s, OCH), 52.0 (s; CH_2N), 31.6 (d, J(C,P) = 29.2 Hz; CH_2P), 30.9 (d, J(C,P) = 26.7 Hz; CH_2P), 27.0 (s; CH_2), 22.6 (s; CH_2), 22.1 ppm (s, CH_3); ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20 °C, H_3PO_4): $\delta = 57.0$ (d, J(P,P) = 34.2 Hz), 37.3 ppm (d, J(P,P) = 34.2 Hz); elemental analysis (%) calcd for $C_{54}H_{52}N_2OP_2Ru$: C 71.43, H 5.77, N 3.09; found: C 70.51, H 5.39, N 2.81.

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