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A Cationic 1-(2-Methylpyridine)Phosphole Cymene Ruthenium Chloride Complex as an Efficient Catalyst in the Transfer Hydrogenation of Ketones

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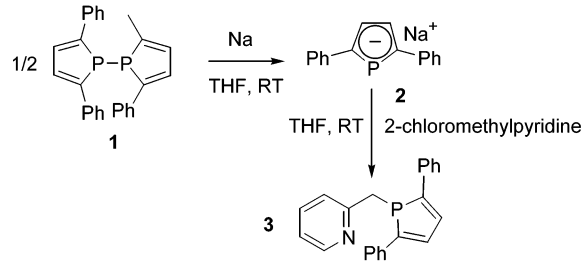
Summary: Reaction of 2,5-diphenylphospholide anion with 2-chloromethylpyridine affords the 1-(2-methylpyridine)phosphole ligand. The corresponding cationic Ru(cymene)Cl chelate complex catalyzes the hydrogen transfer process of ketones with very high TON and TOF numbers.

Due to the presence of two very different binding sites, mixed P, N-chelate ligands possess unusual electronic properties that make them very attractive in both coordination chemistry and catalysis.[1] These ligands, which usually show a pronounced hemilabile character, have found interesting applications in some catalytic processes of recognized importance such as reduction,[2] allylic alkylation,[3] C−C coupling (Heck reaction),[4] and olefin/CO copolymerization.[5] As part of a large research program aimed at incorporating diverse phosphorus heterocycles in mixed heteroditopic chelates and polydentate ligands,[6] we decided to explore the synthesis of 1-phospholyl derivatives of 2-methylpyridine. Herein, we report on the synthesis, the X-ray crystal structure, and the catalytic activity in the transfer hydrogenation of ketones of the cationic cymene RuCl complex of one of these new ligands.

Scheme 1



Among different possible candidates for the phosphole subunit, we selected the 2,5-diphenylphospholyl ligand, whose P-functional derivatives show a very good stability toward air oxidation. Furthermore, the precursor of these P-functional compounds, the 1,2,5-triphenylphosphole, is cheap and easily available on a multigram scale from the simple reaction of dichlorophenylphosphine with 1,4-diphenyl-1,3-butadiene.[7] Synthesis of the 1-(2-methylpyridine)-2,5-diphenylphosphole ligand **3** was carried out following a classical approach that involves the reaction of the 2,5-diphenylphospholide anion **2** with 2-chloromethylpyridine in THF at room temperature. Interestingly, we found that when the easily available 1,1′-bis(2,5-diphenylphosphole)[8] **1** is used as starting precursor of anion **2**, no chromatographic separation is needed to isolate **3**. Following this procedure, ligand **3** was obtained in 80% yield as an air-stable yellow solid which can be stored without special precautions. The formulation of **3** was conventionally established by NMR and mass spectroscopies and elemental analysis (Scheme 1).

As a preliminary study to explore the coordination behavior of **3**, we deliberately focused our work on the synthesis of chelate-based (η^6-arene)ruthenium complexes. Reaction of **3** with half an equivalent of $[\mathrm{Ru}(\eta^6\text{-}C_{10}H_{14})Cl_2]$ did not produce the cationic chelate complex but the monodentate complex **4**, which results from the simple cleavage of the dimer (eq 1). Additionnal heating in different solvents did not allow the displacement of the chloride ligand. Though **4** was fully characterized

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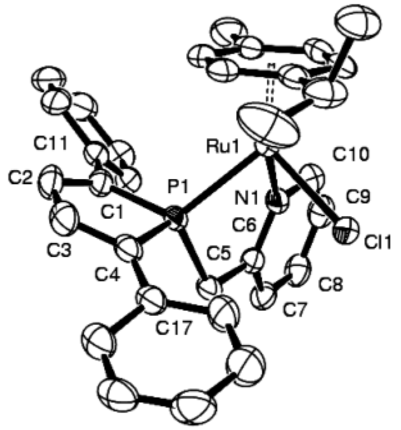
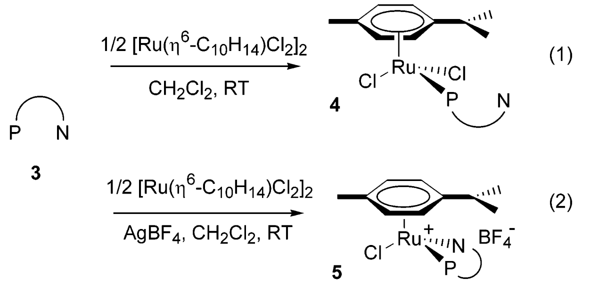


Figure 1. ORTEP view of one molecule of complex **5**. Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the assignment of NMR spectra.

by NMR techniques and elemental analysis, its formulation was definitively established by X-ray crystallography (see Supporting Information available). To force coordination of the pyridine moiety, complex **4** was reacted with the chloride abstractor $AgBF_4$. In this way, complex **5** was quantitatively formed and isolated as an air-stable orange solid. This complex can also be synthesized in a more straightforward way by reacting **3** with the ruthenium dimer in the presence of $AgBF_4$ (eq 2). Complex **5** was fully characterized, and its X-ray crystal structure is presented in Figure 1. As can be seen, the piano-stool geometry of **5** is very classical and does not deserve further comment.



(1)

4

3

(2)

5

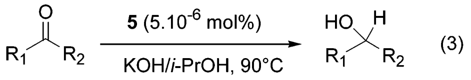
Arene ruthenium complexes are attracting a continuing interest in homogeneous catalysis.[9] A remarkable application is their use in the transfer hydrogenation of ketones.[10] Therefore, as a preliminary test for the catalytic activity of complex **5**, we turn our attention to this process.[11] Though efforts are now focusing on the enantioselective version of this very useful reaction, recent works have showed that the design of highly stable catalysts able to provide high TON and TOF numbers is still a motivating challenge. In this respect, Crabtree and et al. have recently reported on the use of a highly efficient bis-carbene rhodium(III) complex (max. TON = 19 × 10^3 in the conversion of cyclohexanone into cyclohexanol).[12]

Table 1. Transfer Hydrogenation of Ketones Using Complex 5 as Catalyst[a]

entry	substrate	yield (%)[b]	TON[d]	TOF[e]
1	4-heptanone	12 (43)[c]	2.40×10^6	160.0×10^3
2	1,3-diphenylacetone	19 (55)[c]	3.80×10^6	253×10^3
3	cyclohexanone	100	20.0×10^6	1.33×10^6
4	*syn*-2,5-dimethylcyclohexanone	100	20.0×10^6	1.33×10^6
5	acetophenone	90 (100)[c]	18×10^6	1.20×10^6
6	2-acetylepyridine	87 (100)[c]	17.4×10^6	1.16×10^6
7	benzophenone	77 (100)[c]	15.4×10^6	1.026×10^6
8	4-bromoacetophenone	67 (100)[c]	13.4×10^6	893×10^3
9	4-methoxyacetophenone	60 (93)[c]	12.0×10^6	800×10^3
10	4,4′-bismethoxybenzophenone	0 (40)[c]	8×10^{6}[e]	133×10^{3}[f]

[a] Conditions: substrate (3 mmol), catalyst **5** (5 × 10−6 mol %), 15 mL (0.1 M KOH in *i*-PrOH), 90 °C, 15 h. [b]Yields were determined by ^1H NMR or GC. [c]Yield after 60 h. [d]TON = mol product/mol catalyst. [e]TOF = TON/reaction time. [f]TON and TOF calculated for $t = 60$ h.

Typically, complex **5** was reacted at 90 °C with a ketone in the presence of KOH as deprotonating agent and *i*-PrOH, which serves both as solvent and proton source. Interestingly, we found that **5** is highly active in this hydrogenation process (eq 3). Thus, in all



(3)

transformations studied, only a low loading of catalyst (5 × 10^{-6} mol %) was needed to reach very important TON and TOF numbers. As can be seen in Table 1, aliphatic and aromatic ketones can be readily converted to the corresponding secondary alcohols. The highest TON and TOF numbers were obtained in the conversion of cyclic ketones (total conversion, TON = 20 × 10^6, TOF = 1.33 × 10^6 mol h^{-1}). From these data, it is also evident that the electron richness of the aromatic ring strongly influences the rate of conversion, electron rich rings being less reactive (see entries 9 and 10). However, even in these two cases, TONs are higher than those usually obtained using other catalysts.

In summary, we devised an easy access to a new type of mixed phosphole-pyridine ligands. Preliminary experiments indicate that their cationic Ru−(cymene) complexes display a promising catalytic activity in the transfer hydrogenation of ketones. We are now pursuing our studies on these systems in exploring the synthesis of functional derivatives such as tridentate species and the introduction of a chiral center. These results will be reported in due course.

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Supporting Information Available: Text detailing the preparation of compounds **3**−**5**, catalysis protocol, and characterization of products formed and tables of X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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