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Convenient preparation of mononuclear and dinuclear ruthenium hydride complexes for catalytic application

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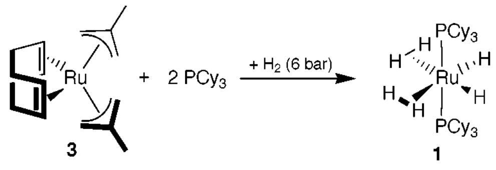
A mixture of commercially available [Ru(cod)(η^3-C_4H_7)$_2$] and PCy_3 reacts with H_2 to give [$RuH_2(H_2)_2(PCy_3)_2$] in high yields, whereas [Ru{$Cy_2P(CH_2)_3PCy_2$}(η^3-C_4H_7)$_2$] leads to [{$Cy_2P(CH_2)_3PCy_2$}RuH(μ-H)$_3$Ru(H_2){$Cy_2P(CH_2)_3PCy_2$}] under identical conditions; this new synthetic procedure provides convenient access to this type of ruthenium hydrides for investigation of their potential in catalytic reactions like the Murai-reaction.

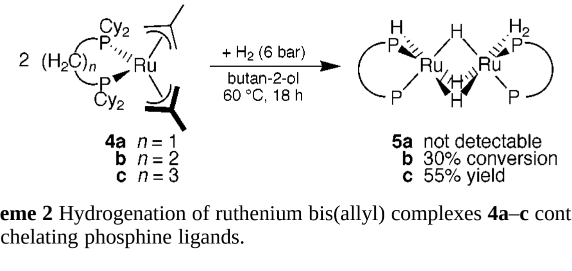
The mononuclear ruthenium hydride [$RuH_2(H_2)_2(PCy_3)_2$] **1**[1,2a] and the related binuclear complex [$(PCy_3)_2$HRu(μ-H)$_3$Ru(H_2)(PCy_3)$_2$] **2**[2] have received considerable attention because of the unique possibility to study η^2-coordinated dihydrogen ligands[3] together with terminal and bridging hydrides in the same coordination sphere. Recent research has demonstrated a remarkable potential of **1** for C–H activation[4] and as a catalyst precursor in C–C bond forming processes, such as olefin metathesis[5] and Murai-type couplings.[6,7]

A major obstacle to a broader investigation of the catalytic properties of **1** and **2** is their time consuming synthesis, involving the highly air sensitive and not readily accessible [Ru(cod)(cot)][8] as a key intermediate. An alternative route to **1** starting from polymeric [Ru(cod)Cl_2]$_n$ was reported recently.[5,9] The generation of complexes $RuH_2L_2(PR_3)_2$ (L = neutral donor ligand) by hydrogenation of [Ru(cod)(η^3-C_4H_7)$_2$)] in the presence of PR_3 and L was described in a patented procedure, but never disclosed in the open literature.[9] None of these methodologies has been applied to the synthesis of derivatives of **1** and **2** bearing chelating bidentate phosphine ligands, which might be of particular interest for catalytic applications.[10]

We now report a very convenient one-step preparation for **1** starting from commercially available [Ru(cod)(η^3-C_4H_7)$_2$)] **3**† (Scheme 1) and the application of the same procedure to the synthesis of derivatives of **2** bearing chelating phosphines (Scheme 2). Preliminary results on the use of **1** in Murai-type coupling reactions are also given.



Scheme 1 One-pot synthesis of **1** by hydrogenation of **3** in the presence of PCy_3.



Scheme 2 Hydrogenation of ruthenium bis(allyl) complexes **4a–c** containing chelating phosphine ligands.

For the synthesis of **1** the air stable components **3** and PCy_3 are placed in a thick-walled glass reactor in 1 : 2 stoichiometry. The reactor is evacuated, purged with argon and the solvent is added. The suspension is pressurised with hydrogen (6 bar) and heated for the appropriate reaction time. After cooling to room temperature, the precipitate is collected by cannula filtration, washed twice with small portions of pentane and dried in a hydrogen stream. Under optimised conditions colourless and spectroscopically pure **1** is obtained in almost quantitative yield (Table 1).

Table 1 Optimisation of reaction parameters for the synthesis of **1**[a]

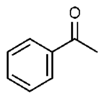
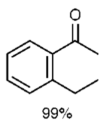
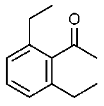
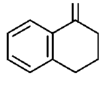
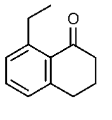
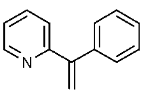
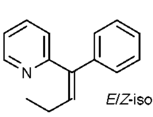
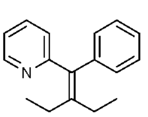
T/°C	Reaction time /h	Yield (%)	Solvent
30	18	47	Pentane
60	18	97	Pentane
60	6	75	Hexane
60	9	85	Butan-2-ol
60	18	93	Butan-2-ol
60	24	83	Butan-2-ol
85	5	74	Butan-2-ol

[a] **3**: 0.375 mmol, PCy_3: 0.75 mmol, solvent: *ca.* 3.5 cm^3.

Applying the same methodology to the mononuclear complex **4c**[11] bearing the chelating dcpp ligand resulted in clean formation of the dinuclear hydride-bridged ruthenium complex **5c**, which was isolated in 55% yield as a bright orange microcrystalline powder (Scheme 2). The structural assignment of **5c** is based on elemental analysis and the excellent agreement of its spectroscopic data with those of **2**.[2]‡

The size of the chelating ring has a strong influence on the reactivity of complexes **4a–c** (Scheme 2): complex **4b** remained

Table 2 Murai-type couplings of sp^2-C–H bonds with ethylene in the presence of **1**[a]

Substrate	T/°C	Conversion[b](%)	Products[b]
	30 50	100 94	 99% 66% +  1% 34%
	30	22	
	30	86	 +  *E/Z*-isomer 74% 26%

[a] Substrate: 0.2 mmol, **1**: 0.02 mmol, ethylene: *ca.* 45 mmol (30 bar), solvent: pentane (2.5 cm^3), $V_{Reactor}$:11 cm^3. [b] Determined by GC–MS analysis after 24 h.

largely unreactive and gave low, but clean conversion to **5b** (< 30%).‡ ^{31}P-NMR monitoring of the reaction of **4a** with H_2 indicated also a very slow reaction. Two different phosphorus containing products were formed, but there were no unambiguously detectable signals in the hydride region of the ^{1}H NMR spectrum.

Preliminary results of some Murai-type couplings using **1** as catalyst precursor are summarised in Table 2. In agreement with Chaudret's recent findings, the alkylation of acetophenone with one molecule of ethylene proceeded smoothly in presence of **1** (10 mol%) under mild conditions.[6]§ Appreciable amounts of the dialkylated product were formed at 50 °C. Most notably, coupling of 2-α-styrylpyridine and ethylene occurred readily to give a mixture of mono- and di-alkylated products at 30 °C. This coupling has been previously reported only for rhodium catalysts under much more forcing conditions.[12]

Further evaluation of the new procedure for the synthesis of ruthenium hydrides and detailed investigation of their catalytic behaviour are under way.

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Notes and references

† [Ru(cod)(η^3-C_4H_7)$_2$] was purchased from Fisher Scientific/ACROS Organics and used as received. For synthesis from [Ru(cod)Cl_2]$_n$, see K. S. MacFarlane, S. J. Rettig, Z. Liu and B. R. James, *J. Organomet. Chem.*, 1998, **557**, 213.

‡ *Characteristic analytical data for* **5c**: δ_H(C_6D_6, 300 MHz) −11.8 (br), δ_P(C_6D_6, 121 MHz) 67.9. ν_{max}(KBr)/cm^{-1} 2105, 1990, 1552. Found: C, 59.43; H, 9.72; P, 13.03. Calc. for $C_{54}H_{106}P_4Ru_2$: C, 59.97; H, 9.88; P, 11.46%. **5b**: δ_H(C_6D_6, 300 MHz) –11.2, δ_P(C_6D_6, 121 MHz) 114.3.

§ We note that the conversion of acetophenone varied between 50 and 100% in several independent catalytic runs. The reason for this is as yet unclear and is part of our current investigations.

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