Disproportionation of Acyclic Ketones to Carboxylate Ions and Ethers: a Poisoning Reaction on the Way to the Chemoselective Reduction of α,β-Unsaturated Ketones to Allylic Alcohols *via* Hydrogen-transfer Catalysed by a Nonclassical Ruthenium(II) Trihydride

Claudio Bianchini,[a] Erica Farnetti,[b] Piero Frediani,[c] Mauro Graziani,[b] Maurizio Peruzzini[a] and Alfonso Polo[a]

[a] *Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi 39, 50132 Firenze, Italy*
[b] *Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste, Italy*
[c] *Dipartimento di Chimica Organica, Università di Firenze, 50131 Firenze, Italy*

The nonclassical trihydride [Ru(tdpep)(H)(H_2)]BPh_4 **1** catalyses under mild conditions the chemoselective reduction of α,β-unsaturated ketones to allylic alcohols *via* hydrogen-transfer [tdpep = $P(CH_2CH_2PPh_2)_3$]; compound **1** reacts with acyclic ketones (or aldehydes) yielding stable η²-carboxylate complexes of general formula [Ru(tdpep)(O_2CR)]BPh_4, and ethers (or ethers plus esters).

In recent years, dihydrogen complexes of late transition metals have been successfully employed in a variety of homogeneous reactions,[1] but their catalytic potential still needs to be examined thoroughly. In this paper, we report on the use of the *cis*-hydride(η²-dihydrogen) complex[2] [Ru(tdpep)(H)(H_2)]BPh_4 **1** [tdpep = $P(CH_2CH_2PPh_2)_3$] as catalyst precursor for the chemoselective reduction of α,β-unsaturated ketones, here exemplified by benzylideneacetone, to the corresponding allylic alcohols *via* hydrogen transfer [eqn. (1)].†

$$PhCH{=}CHCOMe + R^1CH(OH)R^2 \xrightarrow{1} PhCH{=}CHCH(OH)Me + R^1COR^2 \quad (1)$$

As one may readily infer from Table 1, complex **1** catalyses reaction (1) with a selectivity up to 90% and under very mild conditions. When propan-2-ol is employed as hydrogen donor, a slow deactivation of the catalyst occurs, not observed on using cyclopentanol. Interestingly, we have found that the catalyst is poisoned by its reaction with acetone formed in reaction (1) to give the stable η²-acetate complex [Ru(tdpep)(O_2CMe)]BPh_4 **2**‡ and the ether $Me_3COCHMe_2$. A systematic study of the reactions of **1** with symmetrical and asymmetrical ketones has shown the general occurrence of the disproportionation reaction, exemplified in eqn. (2) for acetone ($R^1 = R^2 = Me$) and methyl ethyl ketone ($R^1 = Me$; $R^2 = Et$) [tetrahydrofuran (THF), 20 °C, tenfold excess of ketone, 8 h, argon atmosphere].

$$[Ru(tdpep)(H)(H_2)]^+ + 3\ R^1R^2C{=}O \xrightarrow{-H_2} 1/2\ [Ru(tdpep)(O_2CR^1)]^+ + 1/2\ [Ru(tdpep)(O_2CR^2)]^+ + 1/2\ R^1{}_2R^2COCH(R^1)R^2 + 1/2\ R^2{}_2R^1COCH(R^1)R^2 \quad (2)$$

From the mechanistic viewpoint, there is little doubt that **1** is the precursor to the catalyst [Ru(tdpep)(H)]$^+$ *via* H_2 decoordination. Indeed, the catalytic activity of **1** is almost totally suppressed under 1 atm of H_2 and significantly decreased under N_2 (Table 1), owing to the competing formation of the η¹-dinitrogen complex[2] [Ru(tdpep)(H)(N_2)]BPh_4 **3** in which the N_2 ligand is not easily displaced by ketones.

Having established the importance of H_2 elimination from **1**, a description of the catalysis cycle for the present chemoselective reduction of benzylideneacetone using propan-2-ol or cyclopentanol would not be appropriate as it almost definitely proceeds through the well established mechanism shown in Scheme 1 (cycle **A**).[3]

In contrast, the side reactions leading to the termination η²-carboxylate complexes and ethers are not documented, although one may envisage some similarities with previously reported rhodium- and iridium-catalysed disproportionation reactions of aldehydes into acids and alcohols,[4] and with the Cannizzaro reaction as well.[5]

In the proposed mechanism (see Scheme 1) a crucial role could be played by intermediate **II**, formed by a stepwise reaction involving (*i*) coordination of acetone produced in the catalysis cycle to the unsaturated complex **I**; (*ii*) nucleophilic attack by the *cis*-alkoxy group on the C=O carbon atom of the coordinated acetone. Support of the intermediacy of **II** has been indirectly provided by the reactions of **1** with aldehydes, here MeCHO and EtCHO (THF, 20 °C, tenfold excess of aldehyde, 1 h, argon atmosphere). These reactions give stoichiometric amounts of the corresponding η²-carboxylate complexes, **2** and [Ru(tdpep)(O_2CEt)]BPh_4 **4**,‡ and of the symmetrical ethers $R^1CH_2OCH_2R^1$. Most importantly, appreciable amounts of the corresponding esters $R^1C(O)OCH_2R^1$ ($R^1 = Me$, Et) are also produced, which can be formed through a β-H elimination reaction involving an intermediate of type **II** where R^3 or R^4 is H (Tischenko-type reaction).[5]

Intermediate compounds of type **II** may react with a third molecule of carbonyl compound (ketone or aldehyde) to give

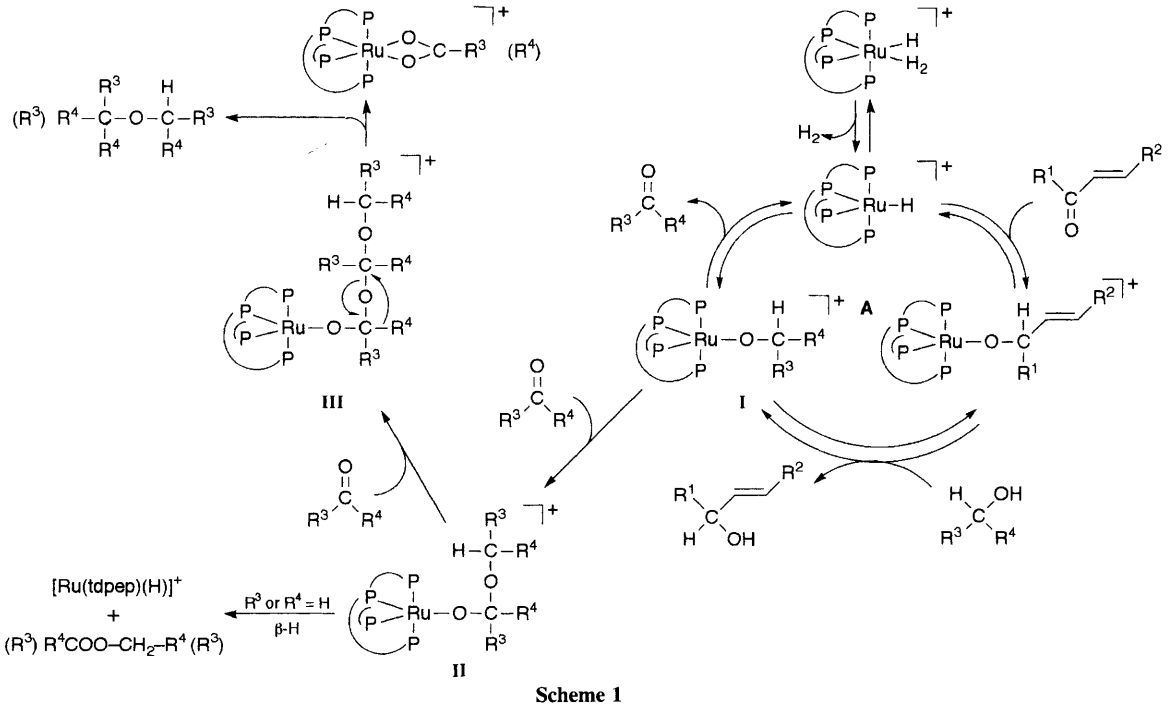
Table 1 Hydrogen transfer reduction of PhCH=CHCOMe to PhCH=CH(OH)Me catalysed by **1**[a]

H_2 donor	Atmosphere[b]	*t*/h	Conversion (%)	Selectivity (%)[c]
Cyclopentanol	Ar	5	95	82
Cyclopentanol	Ar	1	30	89
Propan-2-ol	Ar	1	64	91
Propan-2-ol	Ar	2	85	85
Propan-2-ol	Ar	3	90	83
Propan-2-ol[d]	Ar	1	6	100
Propan-2-ol	N_2	1	36	92
Propan-2-ol	H_2	1	12	92
H_2	H_2	5	0	—
Ethanol	Ar	2	4	100

[a] *Reaction conditions*: [**1**] = 2×10^{-4} mol dm^{-3}; [substrate]/[**1**] = 250; [H_2 donor]/[substrate] = 50; THF (solvent) 10 ml; *T* = 40 °C. [b] 1 atm. [c] Other products: $PhCH_2CH_2COMe$ and $PhCH_2CH_2CH(OH)Me$. [d] Addition of 2 ml of acetone (25 mmol).

† Reaction mixtures were analysed by GC, GC-MS, ^{31}P, ^{13}C and ^1H NMR spectroscopy. Organic compounds (ethers and esters) were identified by comparison with authentic samples.

‡ Satisfactory elemental analyses (C, H, P, Ru) were obtained. *Selected spectroscopic data* in CD_2Cl_2 at 298 K: **2** ^1H NMR (200.1 MHz) δ: 0.77 (br s, $MeCO_2$); $^{13}C\{^1H\}$ NMR (50.3 MHz) δ: 24.8 (CH_3), 187.8 (CO_2); $^{31}P\{^1H\}$ NMR (81.1 MHz) AMQ_2 pattern, δ: 149.4 (dt, P_A, $J_{A\text{-}M}$ 15.5 Hz, $J_{A\text{-}Q}$ 6.5 Hz), 82.9 (td, P_M, $J_{M\text{-}Q}$ 22.2 Hz), 48.9 (dd, P_Q); IR(Nujol mull): ν(CO_2) 1519 cm^{-1}; **4** ^1H NMR (200.1 MHz) δ: 0.12 [t, Me, *J* (Me–CH_2) 7.6 Hz], 1.07 (br q, CH_2); $^{13}C\{^1H\}$ NMR (50.3 MHz) δ: 7.9 (Me), 31.5 (CH_2), 190.6 (CO_2); $^{31}P\{^1H\}$ NMR (81.1 MHz) AMQ_2 pattern, δ: 149.3 (dt, P_A, $J_{A\text{-}M}$ 15.7 Hz, $J_{A\text{-}Q}$ 6.6 Hz), 83.1 (td, P_M, $J_{M\text{-}Q}$ 21.8 Hz), 49.1 (dd, P_Q); IR(Nujol mull): ν(CO_2) 1511 cm^{-1}.



Scheme 1

Ru^{II} products of type **III** which, finally, would decompose to the stable η^2-carboxylate complexes and ethers. The reactions of **1** with aldehydes are much faster than those with ketones, so that the use of primary alcohols as hydrogen donors almost completely suppresses the catalytic activity owing to fast formation of the η^2-carboxylate complexes (Table 1).

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