# Homogeneous catalysis. Use of a ruthenium(II) complex for catalysing the ene reaction

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The complex *trans*-[Ru(salen)(NO)(H$_2$O)]$^+$ catalyses the ene reaction between activated enophiles and olefins to give homoallylic alcohols by a stepwise process.

The oxo-ene reaction, which usually involves the addition of alkenes to aldehydes to produce homoallylic alcohols [eqn. (1)],

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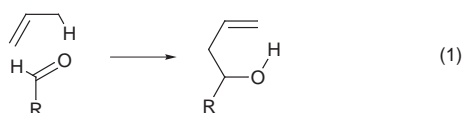
is potentially a useful method of carbon–carbon bond construction.[1] Its implementation, however, suffers from a number of difficiencies. Among these is the necessity of employing high temperatures for most reactions. The obvious method for promoting the reaction at lower temperatures by using conventional Lewis acids such as AlCl$_3$,[2] BF$_3$,[3] SnCl$_4$[4] or TiCl$_4$,[5] can lead to new problems.[1] Whereas these Lewis acids do indeed promote the reaction, they lead to the formation of Lewis acid alcohol intermediates which can release a proton. The released acid can itself act as a catalyst (Prins reaction) and can cause other reactions to occur with the substrates and product. Snider[1,6] has shown that the use of Me$_2$AlCl can promote the ene reaction without proton interference because the methyl groups are capable of rapidly scavenging the proton to give methane. The resultant formation of alkoxide adducts, however, consumes the Lewis acid promoter and, consequently, the Lewis acid is used in stoichiometric or greater quantities. In addition, alkylaluminium halides have been shown to transfer the alkyl group to the aldehyde[7] and to undergo the Oppenauer oxidation.[8] Milder Lewis acids such as those derived from Zn^{II}[9] and Ti^{IV}[10] have been shown to act as true catalysts for a limited number of intramolecular and intermolecular ene reactions, respectively.

Here we report the use of a new type of Lewis acid catalyst for the ene reaction. It is the d^6 ruthenium(II) complex, *trans*-[Ru(salen)(NO)(H$_2$O)] SbF$_6$ **1**, which we have employed for


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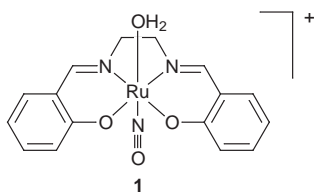
catalysing the Diels–Alder[11] and Mukaiyama reactions.[12] The air and moisture stable catalyst **1** is readily prepared in two steps from commercially available [Ru(NO)Cl$_3$] and the ligand.[11] Although Ru^{II} complexes are generally electron-rich and consequently do not act as Lewis acids, the incorporation of the electron-withdrawing NO$^+$ ligand, the coordination of hard ligands, namely N and O, and the presence of a positive charge all conspire to produce a Lewis acidic ruthenium centre. Further, because the water ligand *trans* to the NO$^+$ ligand is very labile,[11] this coordination site is readily available for binding the enophile (usually an aldehyde) to activate it for reaction and,

after reaction, the homoallylic alcohol product is expected to be labile for efficient turnover.

Some of these results are collected in Table 1. As is commonly observed for Lewis acid promotion, only electron-difficient carbonyl-containing enophiles engage in the ene reaction at acceptable rates. Generally, ruthenium(II) aquo complexes are weak acids having a pK_a similar to AcOH acid (in water).[13] In order to determine the ability of acid to promote the reactions, 2 mol% TFA was used under the same conditions to promote the reaction shown in entry 1 (Table 1). It was found that < 1% conversion to the ene product occurred after 150 h, indicating that acid is neither responsible for, nor competitive with, the ruthenium catalysed process.

Although, like other promoters, the ruthenium catalyst has its limitations for the ene reaction, it serves to demonstrate that structurally defined transition metal complexes which are not normally oxophilic can be modified to act as genuine catalysts for the generally resistant ene reaction. It is probable, however, that the present catalyst will find practical applications in the intramolecular ene reaction. The conversion of (+)-citronellal to *l*-isopulegol [eqn. (2)] is an important step in the industrial
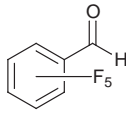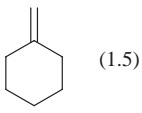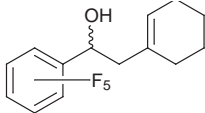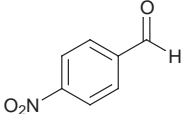

$$(2)$$
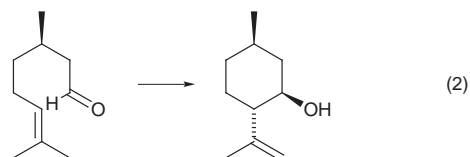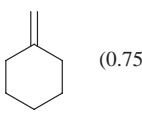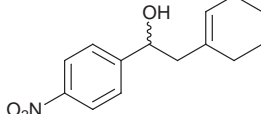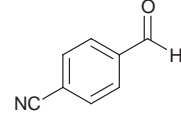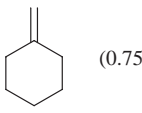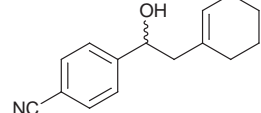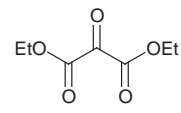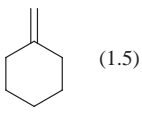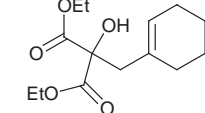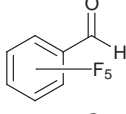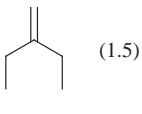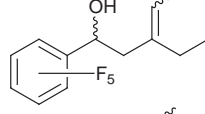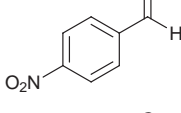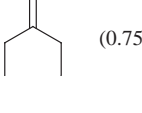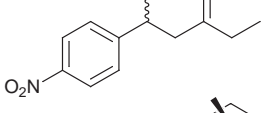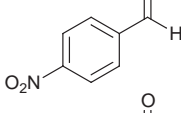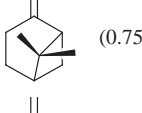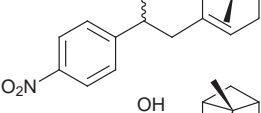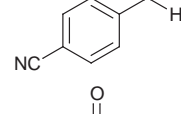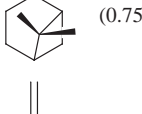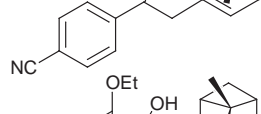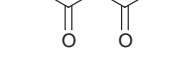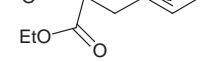
production of *l*-menthol[14] where ZnBr$_2$ in stoichiometric amounts at *ca.* 5 °C is used to give *l*-isopulegol in 95% yield over the other isomers. Using 1 mol% of the ruthenium catalyst in MeNO$_2$ at 25 °C, (+)-citronellal is converted to *l*-isopulegol after 6 h. An 80% yield of *l*-isopulegol was obtained, with the remaining product consisting of the other (three) isomers.[9,14,15] Given this efficient conversion, it is possible to entertain the prospect of using chiral analogues of the present catalyst for asymmetric catalytic intramolecular ene reactions.

In order to ascertain if the present catalysed ene reactions are concerted or stepwise processes we have investigated the products from a number of 1,3-dienes. A typical transformation is illustrated in eqn. (3), together with the putative inter-

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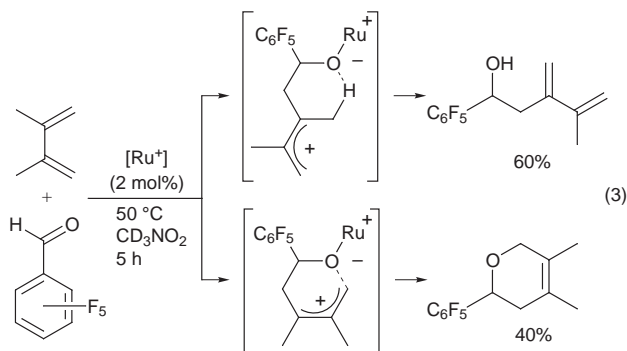
mediates. The two products are formed in constant kinetic proportions and are not interconverted in the presence of the

Table 1 Catalytic ene reaction using **1** (2 mol%) in MeNO$_2$ at 50 °C

Entry	Enophile (0.5 M)	Olefin (conc./M)	Product	Isomer ratio[a]	t/h[b]	Isolated yield (%)
1	C$_6$F$_5$CHO	(1.5)		—	5	88[c]
2	4-O$_2$N-C$_6$H$_4$CHO	(0.75)		—	10	83[c]
3	4-NC-C$_6$H$_4$CHO	(0.75)		—	50	82[c]
4	EtO$_2$C-CO-CO$_2$Et	(1.5)		—	42	59
5	C$_6$F$_5$CHO	(1.5)		56:44	5	85[c]
6	4-O$_2$N-C$_6$H$_4$CHO	(0.75)		66:34	40	75[c]
7[d]	4-O$_2$N-C$_6$H$_4$CHO	(0.75)		81:19	24	47
8[d]	4-NC-C$_6$H$_4$CHO	(0.75)		78:22	41	45
9[d]	EtO$_2$C-CO-CO$_2$Et	(1.5)		—	37	35

[a] Isomers not assigned. [b] Time required for >95% reaction of enophile. [c] Only the pure product is formed by ^{1}H NMR spectroscopy. [d] In [^{2}H$_6$]acetone.

catalyst. The formation of the two products [eqn. (3)] suggests that the ene reaction with the 1,3-diene may occur *via* a non-concerted process where the carbenium ion has sufficient lifetime to promote either the ene reaction or the hetero-Diels–Alder reaction. Although it is recognized that the allylic cation may have a greater stability than a localized carbenium ion formed by monoolefins, the formation of the two products when 1,3-dienes are used indicates that in the present systems the monoolefin ene reactions could proceed by carbenium ion intermediates.[16]

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Notes and References

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