Electronic Supplementary Information

New insight into the role of a base in the mechanism of imine transfer hydrogenation on a Ru(II) half-sandwich complex

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Contents:

1) NMR data

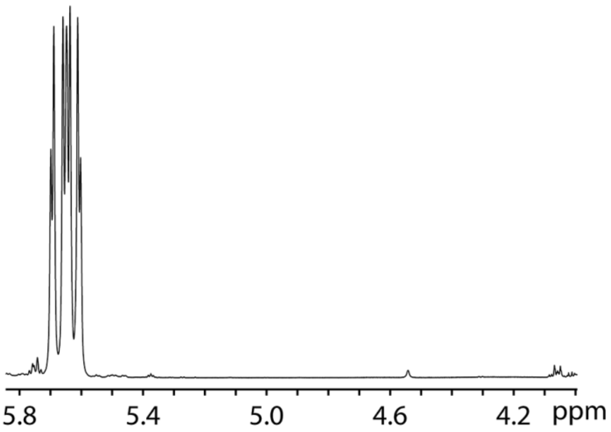


Fig. S1 ^{1}H spectrum of [RuCl(η^6-*p*-cymene)TsDPEN] (**1**) in CD_3CN showing the aromatic signals of *p*-cymene.

Table S1 Direct $^1J_{C–H}$ coupling constants of aromatic C–Hs in *p*-cymene.

$^1J_{C–H}$ [Hz]	
RuCl(*p*-cym)TsDPEN][a]	RuH(*p*-cym)TsDPEN][a]
176	169
175	171
175	172
179	171

[a] *p*-cym = η^6-*p*-cymene.

2) ESI$^+$-FT-ICR MS spectra

2.1 Additional measurement with TEA

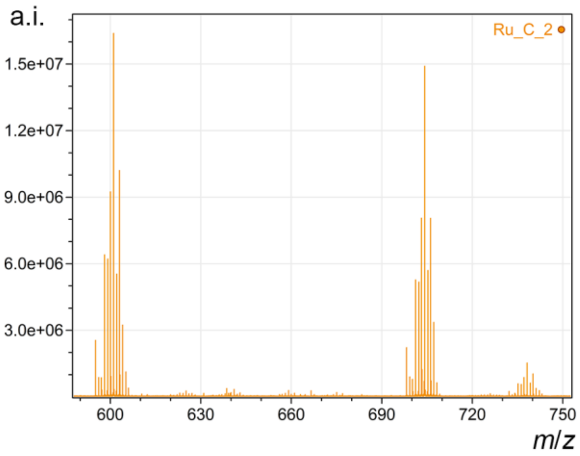
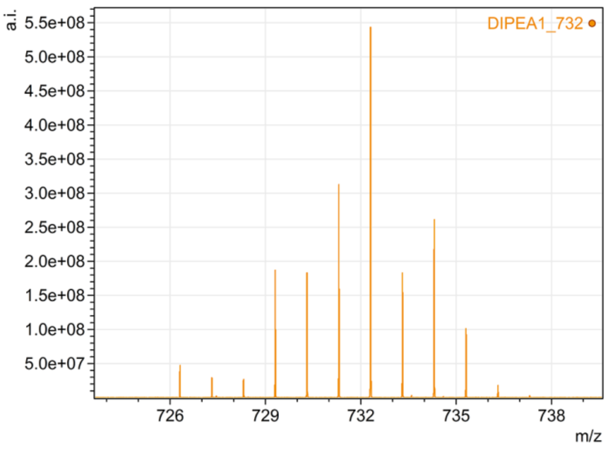


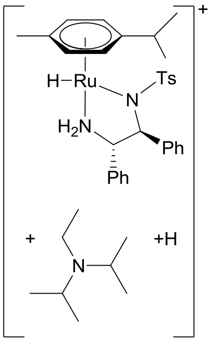
Fig. S2 ESI$^+$-FT-ICR MS spectrum of **1** in presence of HCOOH and TEA after a 1000-fold dilution with CH_3CN.

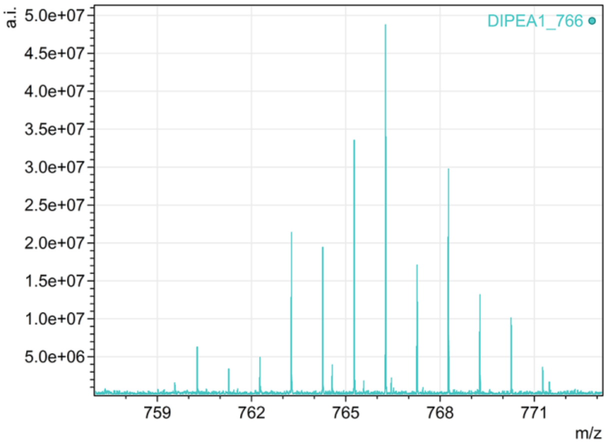
2.1 Measurement with diisopropylethylamine



$C_{39}H_{56}N_3O_2SRu$

m/z (calculated)	726.3164
m/z (measured)	726.3150





$C_{39}H_{55}N_3O_2SRuCl$

m/z (calculated)	760.2779
m/z (measured)	760.2756

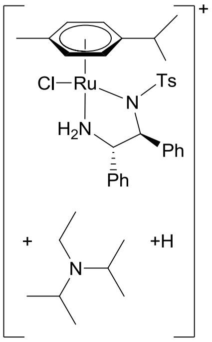


Fig. S3 Details of ESI$^+$-FT-ICR MS spectrum of **1** in presence of HCOOH and diisopropylethylamine.

2.2 Measurement with 1,4-diazabicyclo[2.2.2]octane (DABCO)

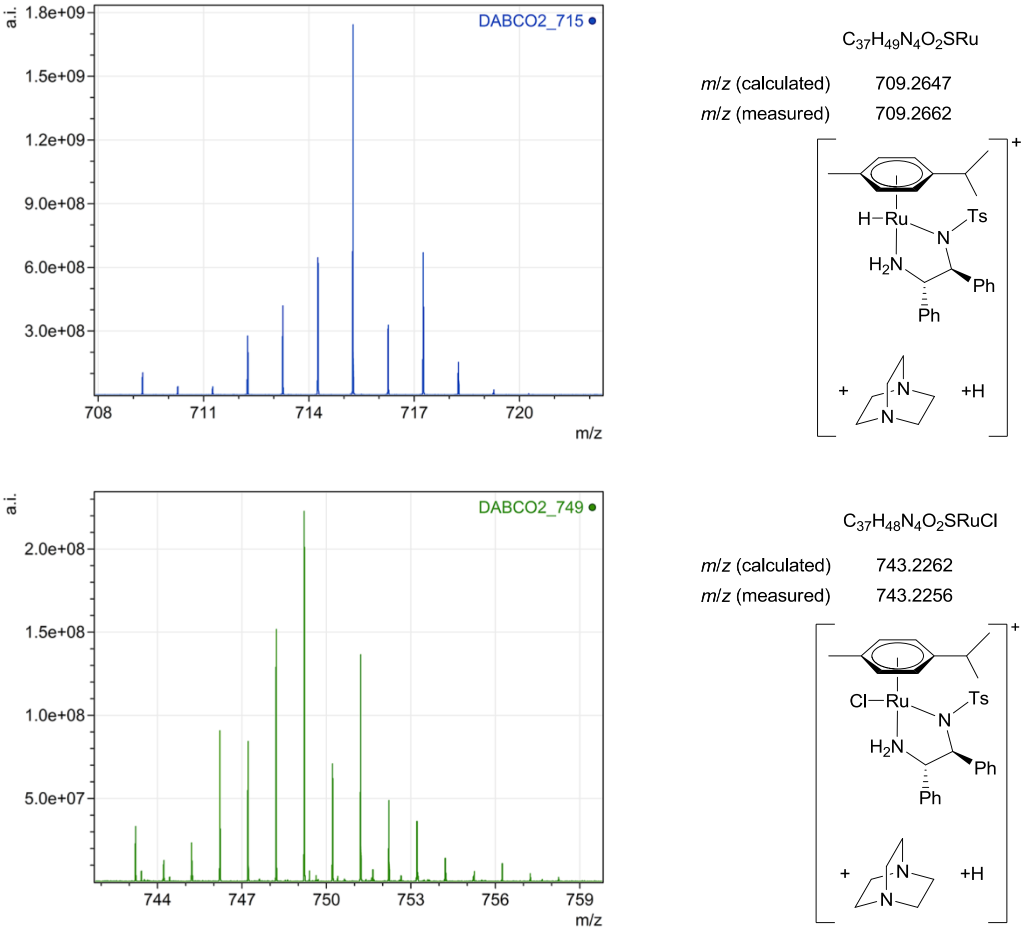


Fig. S4 Details of ESI$^+$-FT-ICR MS spectrum of **1** in presence of HCOOH and 1,4-diazabicyclo[2.2.2]octane (DABCO).

3) Additional assignment of VCD signal

This spectral assignment complements the main text of the article and relates to Fig. 4.

In the IR absorption spectrum within 1550−1750 cm^{-1}, vibrations of the formate anion, formic acid and protonated piperidine emerged when the HCOOH/base mixture was added to **1** in DMSO-*d*$_6$. The broad bands were a result of an ongoing reaction in the mixture during which the amount of formic acid, formate anion and protonated species were changing. In the IR absorption spectrum of **1**, the bands in the range of 1610−1430 cm^{-1} were assigned to the C=C vibrations of the aromatic rings. The corresponding signals were also present in VCD spectra within 1550−1430 cm^{-1}. In the samples containing **1** together with the HCOOH/TEA and HCOOH/piperidine mixtures, no significant changes of these bands were observed.

An absorption band at 1385 cm^{-1} in the spectrum of **1** was assigned to a combined deformation vibration of CH_3 groups. The increase of the signal upon the addition of the HCOOH/base mixture was accompanied by a new band which appeared at 1329 cm^{-1} and 1333 cm^{-1} for piperidine and TEA, respectively, representing deformation vibrations of the CH_2 and CH_3 groups of the bases.

4) FT-IR spectra within 4000–2000 cm^{-1}

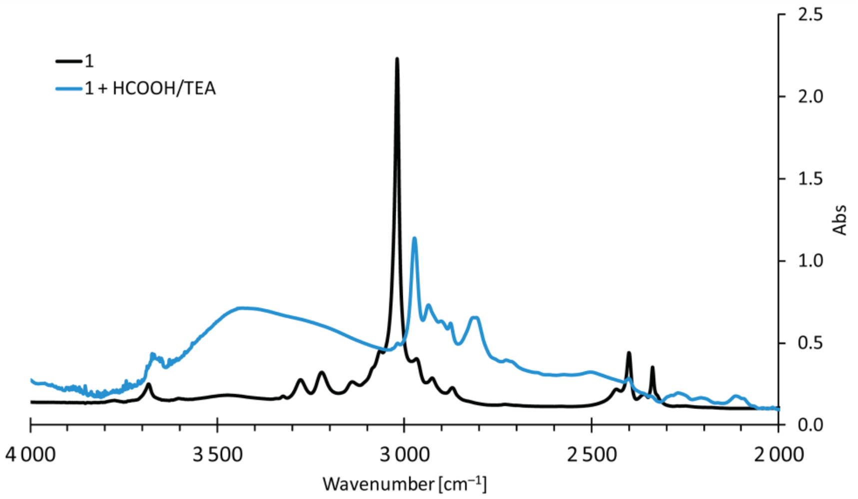


Fig. S5 FT-IR spectra of **1** and **1** + HCOOH/TEA.