Electronic Supplementary Information for Dalton Transactions

trans-$Fe^{II}(H)_2$(diphosphine)(diamine) complexes as alternative catalysts for the asymmetric hydrogenation of ketones? A DFT study

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Supporting Computational Data

Due to the large number of atoms in the optimized structures it is unfeasible to present XYZ coordinates in the table format. Instead, we have included all necessary XYZ files in the Zip- archive. The content of tables is as follows:

Table of Content

A. Based on Table 1: Comparison of Structural Conformations

Table A Electronic energies between the *trans*- and *cis*- isomers of the [$M(H)_2$(*S*-xylbinap)(*S*,*S*-dpen)] and [$M(H)_2$(*S*-BINAP)(*S*,*S*-dpen)] complexes, where M = Ru and Fe.

Level of Theory	Basis Set		$Ru^{II}(H)_2$(diphosphine)(S,S-dpen)		$Fe^{II}(H)_2$(diphosphine)(S,S-dpen)	
			XylBINAP	BINAP	XylBINAP	BINAP
			E [hartrees]			
PBE	DNP	*trans*	-3470.30091370	-3156.09229030	-3487.56174970	-3173.35331800
		cis	-3470.29373690	-3156.08585710	-3487.54886050	-3173.34191670
PBE	6-31G **/ LANL2DZ	*trans*	-3437.22883146	-3123.12551219	-3466.73778810	-3152.63437597
		cis	-3437.22531492	-3123.12230077	-3466.73189327	-3152.62862365
PBE0	6-31G **/ LANL2DZ	*trans*	-3437.60051060	-3123.42781561	-3467.05788122	-3152.88512492
		cis	-3437.59421349	-3123.42183393	-3467.04447814	-3152.87192947
B3LYP	6-31G **/ LANL2DZ	*trans*	-3441.02152492	-3126.46293057	-3470.52370552	-3155.96495900
		cis	-3441.01676916	-3126.45879427	-3470.51062337	-3155.95234981

Below are relative XYZ files, shown in the attached Zip-archive.

A-1 $DMol^3$/PBE/DNP

A11. *trans*-[$Ru^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A12. *cis*-[$Ru^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A13. *trans*-[$Ru^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]
A14. *cis*-[$Ru^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]
A15. *trans*[-$Fe^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A16. *cis*-[$Fe^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A17. *trans*-[$Fe^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]
A18. *cis*-[$Fe^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]

A-2 Gaussian03/PBE/6-31G**/LANL2DZ

A21. *trans*-[$Ru^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A22. *cis*-[$Ru^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A23. *trans*-[$Ru^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]
A24. *cis*-[$Ru^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]
A25. *trans*[-$Fe^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A26. *cis*-[$Fe^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A27. *trans*-[$Fe^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]
A28. *cis*-[$Fe^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]

A-3 Gaussian03/PBE0/6-31G**/LANL2DZ

A31. *trans*-[$Ru^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A32. *cis*-[$Ru^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A33. *trans*-[$Ru^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]
A34. *cis*-[$Ru^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]
A35. *trans*[-$Fe^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A36. *cis*-[$Fe^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A37. *trans*-[$Fe^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]
A38. *cis*-[$Fe^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]

A-4 Gaussian03/B3LYP/6-31G**/LANL2DZ

A41. *trans*-[$Ru^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A42. *cis*-[$Ru^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A43. *trans*-[$Ru^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]
A44. *cis*-[$Ru^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]
A45. *trans*[-$Fe^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A46. *cis*-[$Fe^{II}(H)_2$(*S*-XylBINAP)(*S*,*S*-dpen)]
A47. *trans*-[$Fe^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]
A48. *cis*-[$Fe^{II}(H)_2$(*S*-BINAP)(*S*,*S*-dpen)]

B. Based on Table 2: Comparison of Spin States

Table B Electronic energies of the *trans*-[$Ru^{II}(H)_2$(*S*-xylbinap)(*S*,*S*-dpen)] and *trans*-[$Fe^{II}(H)_2$(*S*-xylbinap)(*S*,*S*-dpen)] complexes with S=0, 2, and 4.

Spin Multiplicity	Ru-XylBINAP	Fe-XylBINAP
	E [hartrees]	
Singlet	-3470.2639053	-3487.5236447
Triplet	-3470.1966383	-3487.4802138
Quintet	-3470.1077703	-3487.4320404

Below are relative XYZ files, shown in the attached Zip-archive.

B. DMol^3/PBE/DNP

B1. *trans*-[$Ru^{II}(H)_2$(*S*-xylbinap)(*S*,*S*-dpen)]– Singlet
B2. *trans*-[$Ru^{II}(H)_2$(*S*-xylbinap)(*S*,*S*-dpen)] – Triplet
B3. *trans*-[$Ru^{II}(H)_2$(*S*-xylbinap)(*S*,*S*-dpen)] – Quintet

B4. *trans*-[$Fe^{II}(H)_2$(*S*-xylbinap)(*S*,*S*-dpen)] – Singlet
B5. *trans*-[$Fe^{II}(H)_2$(*S*-xylbinap)(*S*,*S*-dpen)] – Triplet
B6. *trans*-[$Fe^{II}(H)_2$(*S*-xylbinap)(*S*,*S*-dpen)] – Quintet

C. Based on Table 3 and Figure 2: Whole Catalytic Cycles in Simplifed Systems

Table C The electric energies (in hartrees) of reactant, TS, and product for the H_2-hydrogenation of acetone catalysed by *trans*-$[M^{II}(H)_2(PH_3)_2(en)]$ model catalysts, where M = Ru and Fe.

Functional	PBE	PBE	PBE0	B3LYP	mPW1PW91
Basis Set	DNP	6-31G **	6-31G **	6-31G **	6-31G**
	N/A	LAND2DZ	LAND2DZ	LAND2DZ	SDD
$E_{Ru,\ H2\text{-}Transfer,Rac}$	-1164.26200780	-1196.55122960	-1164.34210311	-1165.12374393	-1166.09124300
$E_{Ru,\ H2\text{-}Transfer,TS}$	-1164.25858000	-1196.55473000	-1164.33769000	-1165.11832938	-1166.08696625
$E_{Ru,\ H2\text{-}Transfer,Pro}$	-1164.27783649	-1196.56547550	-1164.35729089	-1165.13677073	-1166.10291681
$E_{Ru,\ H2\text{-}Split,Rac}$	-1003.52607400	-971.31812421	-971.37115790	-971.93508966	-972.94276847
$E_{Ru,\ H2\text{-}Split\ ,TS}$	-1003.51106900	-971.30260316	-971.35777253	-971.91315786	-972.92892000
$E_{Ru,\ H2\text{-}Split\ ,Pro}$	-1003.54132350	-971.33261145	-971.39466548	-971.94956287	-972.96704523
$E_{Fe,\ H2\text{-}Transfer,Rac}$	-1213.81182060	-1193.77010136	-1193.79858433	-1194.62549177	-1195.00752196
$E_{Fe,\ H22\text{-}Transfer,TS}$	-1213.80860000	-1193.76692000	-1193.79475000	-1194.62043710	-1195.00382898
$E_{Fe,\ H2\text{-}Transfer,Pro}$	-1213.82691190	-1193.78690418	-1193.81450050	-1194.64003965	-1195.02283078
$E_{Fe,\ H2\text{-}Split,Rac}$	-1020.79219140	-1000.83011247	-1000.83141714	-1001.43909777	-1001.86446393
$E_{Fe,\ H2\text{-}Split\ ,TS}$	-1020.77919000	-1000.81538361	-1000.81856000	-1001.41870838	-1001.85085000
$E_{Fe,\ H2\text{-}Split\ ,Pro}$	-1020.80302440	-1000.84137447	-1000.85190975	-1001.45212437	-1001.88441044

- $\Delta E_{M,\ H2\text{-}Transfer,X}$ is the electric energy hydrogen transfers in the acetone/isopropanol reaction catalysed by the 18-electron hydride-amino metal complex;
- $\Delta E_{M,\ H2\text{-}Split,X}$ is the electric energy for the heterolytic dihydrogen splitting on the 16-electron hydrido-amido metal complex.
- M = Ru and Fe; X = Rac, TS, and Pro which stand for Reactant, Transition-State Structure, and Product, respectively.

Below are relative XYZ files, shown in the attached Zip-archive.

C-1 DMol^3/PBE/DNP

C11Ru-Re. *trans*-$[Ru^{II}M(H)_2(PH_3)_2(en)]$ H_2-Transfer,Rac
C11Ru-TS. *trans*-$[Ru^{II}M(H)_2(PH_3)_2(en)]$ H_2-Transfer,TS
C11Ru-Pr. *trans*-$[Ru^{II}M(H)_2(PH_3)_2(en)]$ H_2-Transfer,Pro
C12Ru-Re. *trans*-$[Ru^{II}M(H)_2(PH_3)_2(en)]$ H_2-Split,Rac
C12Ru-TS. *trans*-$[Ru^{II}M(H)_2(PH_3)_2(en)]$ H_2-Split,TS
C12Ru-Pr. *trans*-$[Ru^{II}M(H)_2(PH_3)_2(en)]$ H_2-Split,Pro

C11Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Rac
C11Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,TS
C11Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Pro
C12Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Rac
C12Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,TS
C12Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Pro

C-2 Gaussian03/PBE/6-31G/LANL2DZ**

C21Ru-Re. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Rac
C21Ru-TS. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,TS
C21Ru-Pr. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Pro
C22Ru-Re. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Rac
C22Ru-TS. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,TS
C22Ru-Pr. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Pro

C21Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Rac
C21Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,TS
C21Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Pro
C22Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Rac
C22Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,TS
C22Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Pro

C-3 Gaussian03/PBE0/6-31G/LANL2DZ**

C31Ru-Re. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Rac
C31Ru-TS. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,TS
C31Ru-Pr. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Pro
C32Ru-Re. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Rac
C32Ru-TS. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,TS
C32Ru-Pr. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Pro

C31Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Rac
C31Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,TS
C31Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Pro
C32Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Rac
C32Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,TS
C32Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Pro

C-4 Gaussian03/B3LYP/6-31G/LANL2DZ**

C41Ru-Re. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Rac
C41Ru-TS. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,TS
C41Ru-Pr. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Pro
C42Ru-Re. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Rac
C42Ru-TS. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,TS
C42Ru-Pr. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Pro

C41Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Rac
C41Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,TS
C41Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Pro
C42Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Rac
C42Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,TS
C42Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Pro

C-5 Gaussian03/B3LYP/6-31G/SDD**

C51Ru-Re. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Rac
C51Ru-TS. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,TS
C51Ru-Pr. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Pro
C52Ru-Re. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Rac
C52Ru-TS. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,TS
C52Ru-Pr. *trans*-[$Ru^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Pro

C51Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Rac
C51Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,TS
C51Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Transfer,Pro
C52Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Rac
C52Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,TS
C52Fe. *trans*-[$Fe^{II}M(H)_2(PH_3)_2(en)$] H_2-Split,Pro

D. Based on Figure 5: H_2-Transfer in Real Systems

There are seven real structures in the Ru system and Fe systems, respectively. The XYZ files are shown in the attached Zip-archive.

D. DMol^3/PBE/DNP

D01. [Acetophenone + 18e- dihydride-amino Ru^{II} complex]
D02. INT-I_{Ru}
D03. INT-II_{Ru}
D04. Hydrog. TS_{Ru}
D05. ADDUCT-I_{Ru}
D06. ADDUCT-II_{Ru}
D07. [Phenylenthanol + 16e- hydrido-amido Ru^{II} complex]

D08. [Acetophenone + 18e- dihydride-amino Fe^{II} complex]
D09. INT-I_{Fe}
D10. INT-II_{Fe}
D11. Hydrog. TS_{Fe}
D12. ADDUCT-I_{Fe}
D13. ADDUCT-II_{Fe}
D14. [Phenylenthanol + 16e- hydrido-amido Fe^{II} complex]