Supplementary Material

Tridentate and Tetradentate Iminophosphorane-Based Ruthenium Complexes in Catalytic Transfer Hydrogenation of Ketones.

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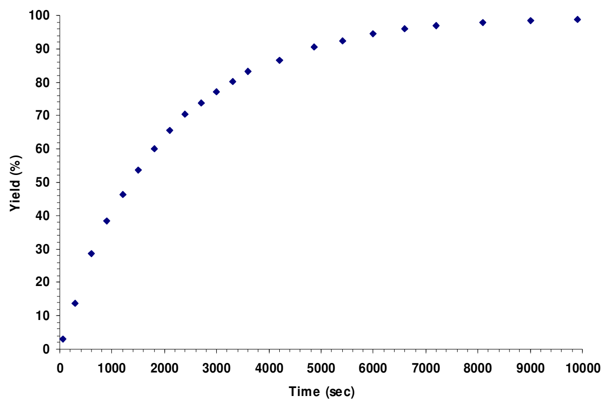
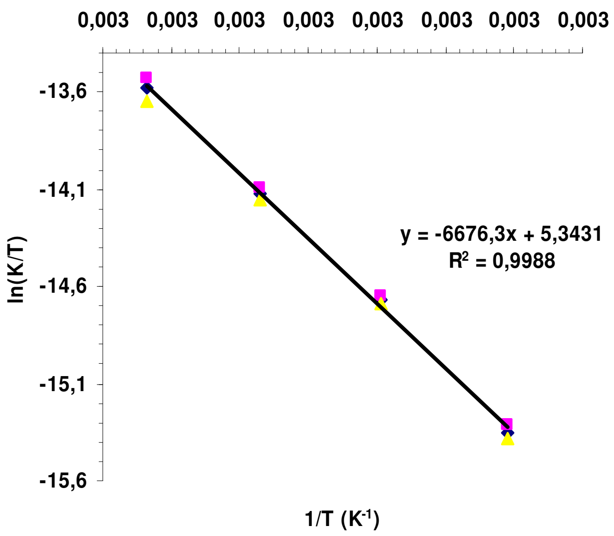
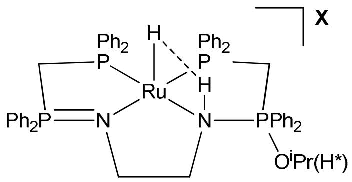
1. **Figure S1:** Conversion of acetophenone, expressed as a percentage yield, as a function of time with **6**.



2. **Figure S2:** Graph of ln(K/T) vs 1/T with **6.**



3. **Figure S3:** Schematic representation of a postulated intermediate.



In light of the similar kinetics and chemeoselectivity observed for **6** and **3** one could postulate an outer sphere hydride transfer assisted by the ligand, with reformation of the Ru-H facilitated by the presence of the isoproxide anion in solution. Unfortunately evidence of the formation of a P-O^{i}Pr functionality could not be detected spectroscopically (^{31}P and ^{1}H NMR where applicable) at ambient temperature or at 345K upon stoichiometric reaction of **5** and **6** with excess NaO^{i}Pr in THF-d_8 and in ^{i}PrOH.

4. **Table S1.** Influence of PCy_3 on the catalytic hydrogenation of acetophenone with **6** as precatalyst.

	Conversion (%)				
Entry	20 min	40 min	60 min	80 min	120 min
1[a]	38	58	68	76	87
2[b]	32	57	72	81	91

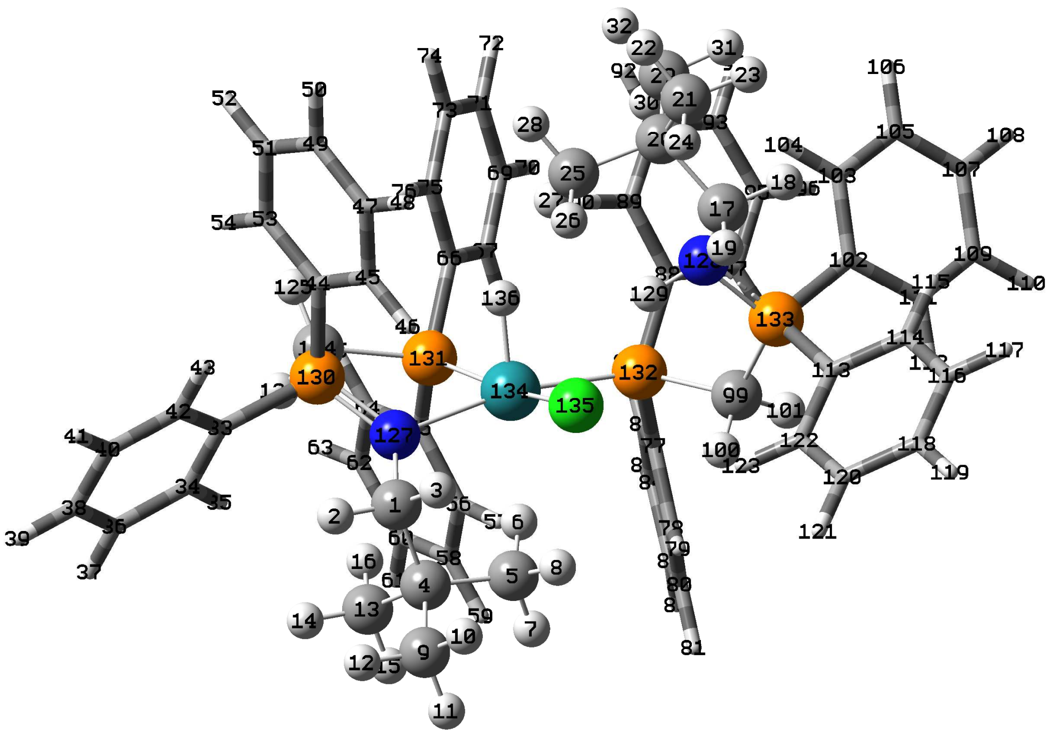
[a] Conditions: 100 equiv of acetophenone (146 μL, 1.25 mmol), 10 equiv Na (2.9 mg, 0.125 mmol), 100 equiv of the internal standard veratrole (160 μL, 1.25 mmol) and 1 equiv of **6** (0.0125 mmo) in 5 mL of ^{i}PrOH at 80 ºC.[b] Conditions: same as for those for footnote [a] but with the addition of 10 equivalents of PCy_3.

5. Complete Gaussian reference

Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004

6. ONIOM optimisation for 7 and Cartesian coordinates.

In the structure below the MM part is represented with tubes whereas the MQ part with ball and bonds.



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	10061003	-2.886584	-1.577216	-2.268543
2	1	10011000	-3.816417	-2.163493	-2.323450
3	1	10011000	-2.064937	-2.275796	-2.464517
4	6	10061003	-2.932039	-0.515784	-3.393183
5	6	10061003	-1.614456	0.260513	-3.445888
6	1	10011000	-1.361290	0.701668	-2.456759
7	1	10011000	-1.679373	1.108713	-4.138345
8	1	10011000	-0.776247	-0.377921	-3.737723
9	6	10061003	-3.117897	-1.262701	-4.723135
10	1	10011000	-2.308547	-1.982926	-4.893787
11	1	10011000	-3.125753	-0.561596	-5.566066
12	1	10011000	-4.068251	-1.810655	-4.741246
13	6	10061003	-4.100966	0.450920	-3.181795
14	1	10011000	-5.062862	-0.076692	-3.213556
15	1	10011000	-4.122837	1.215984	-3.966780
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17	6	10061003	3.772237	-2.893573	0.467198
18	1	10011000	4.826557	-2.654728	0.660454
19	1	10011000	3.742415	-3.572948	-0.397780
20	6	10061003	3.196140	-3.625028	1.694672

21	6	10061003	3.967756	-4.949877	1.802022
22	1	10011000	3.620703	-5.521023	2.670290
23	1	10011000	5.045046	-4.781907	1.927574
24	1	10011000	3.821548	-5.576523	0.913681
25	6	10061003	1.704996	-3.913204	1.492152
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