Supporting Information

# Titanocene(III) complexes with 2phosphinoaryloxide ligands for the catalytic dehydrogenation of dimethylamine borane

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## X-ray analysis



**Figure S1.** Molecular structure of compound **3b**. The thermal ellipsoids correspond to 30% probability. Hydrogen atoms and co-crystallized toluene are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1-O1 2.0498(12), Ti1-P1 2.6170(5), Ti1-O1-C1 128.25(10).



**Figure S2.** Molecular structure of compound **5b**. The thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1-O1 1.9200(9), Ti1-O1-C1 147.59(9).

	3a	3b	5a	5b
Chem. Formula	C <sub>22</sub> H <sub>28</sub> OPTi	C <sub>28</sub> H <sub>24</sub> OPTi	C <sub>32</sub> H <sub>48</sub> OPTi	C <sub>38</sub> H <sub>46</sub> OPTi
Form. wght.	387.31	501.41	527.57	595.60
Color	green	green	brown	green
Cryst syst	orthorhombic	triclinic	monoclinic	monoclinic
Space group	$Pna2_1$	pl	$P2_l/n$	$P2_{1}/n$
a [Å]	20.1401(7)	8.9793(2)	17.2942(4)	12.8912(4)
b [Å]	9.5333(3)	9.9618(2)	10.2289(3)	16.8203(5)
c [Å]	10.0967(3)	15.3438(4)	18.3519(5)	15.6003(5)
α [deg]	90	100.246(1)	90	90
β [deg]	90	94.705(1)	110.637(1)	107.636(2)
γ [deg]	90	112.776(1)	90	90
V [Å <sup>3</sup> ]	1938.58(11)	1227.96(5)	3038.14(14)	3223.69(17)
Ζ	4	2	4	4
Density [g·cm <sup>-3</sup> ]	1.327	1.356	1.153	1.227
μ(Mo Kα) [mm <sup>-1</sup> ]	0.531	0.437	0.356	0.343
T [K]	150(2)	150(2)	150(2)	150(2)
No. of rflns (measd)	31709	49888	76231	78374
No. of rflns (indep)	4558	5645	7341	7780
No. of rflns (obsd)	4058	5018	6345	6588
No. of params	214	331	326	380
GOF on $F^2$	1.029	1.061	1.038	1.048
$R_1(I \ge 2\sigma(I))$	0.0354	0.0350	0.0345	0.0310
$wR_2$ (all data)	0.0853	0.0920	0.0947	0.0873

Table S1. Crystal data and structure refinement parameters of 3a, 3b, 5a and 5b.

### **Volumetric curves**

The volumetric curves for low hydrogen evolutions show an exceptional behaviour, which is caused by the experimental setup: The sensor, which records pressure changes due to gas evolution, is very sensitive and is thus prone to very small changes of the laboratory pressure and temperature. This affects the shape of the curves. Details of the experimental setup were published before in: H.-J. Drexler, A. Preetz, T. Schmidt and D. Heller, in *The Handbook of Homogeneous Hydrogenation*, Vol. 1 (Eds.: J. G. De Vries, C. J. Elsevier), Wiley-VCH, Weinheim, 2007, pp. 257.



Figure S3. Hydrogen evolution curve for 3a in neat 6 (T = 50 °C, 2 mol% catalyst).



Figure S4. Hydrogen evolution curve for 3a in toluene (T = 25 °C, 2 mol% catalyst).



Figure S5. Hydrogen evolution curve for 3b in neat 6 (T = 50 °C, 2 mol% catalyst).



Figure S6. Hydrogen evolution curve for 3b in toluene (T = 25 °C, 2 mol% catalyst).



Figure S7. Hydrogen evolution curve for 5a in neat 6 (T = 50 °C, 2 mol% catalyst).



Figure S8. Hydrogen evolution curve for 5a in toluene (T = 25 °C, 2 mol% catalyst).



Figure S9. Hydrogen evolution curve for 5b in neat 6 (T = 50 °C, 2 mol% catalyst).



Figure S10. Hydrogen evolution curve for 5b in toluene (T = 25 °C, 2 mol% catalyst).



Figure S11. Hydrogen evolution curve for neat 6 (T = 50 °C, without catalyst).

#### Example for GC analysis of the gas volume

Data File C:\CHEM32\1\DATA\0214\0328000001.D Sample Name: 214



Figure S12. GC analysis of a dehydrogenation experiment. Note that hydrogen is the only gaseous product (t = 5.960 min), the peak at t = 9.657 min is due to residual air present in the syringe.

# NMR spectroscopy



**Figure S13.** <sup>1</sup>H NMR spectra for dehydrogenation of **6** by **3a** in  $C_6D_6$  at 80 °C (300 MHz; blue: two equivalents of **6**, red: after addition of eight equivalents of **6**, green: after addition of ten equivalents of **6**, purple: control for complete conversion).



Figure S14. <sup>11</sup>B NMR spectra for dehydrogenation of **6** by **3a** in  $C_6D_6$  at 80 °C resulting in formation of **7**, **8**, **10** and the unknown boron species \* (96 MHz; blue: two equivalents of **3**, red: after addition of eight equivalents of **6**, green: after addition of ten equivalents of **6**, purple: control for complete conversion).



**Figure S15.** <sup>31</sup>P NMR spectrum for dehydrogenation of 6 by **3a** in  $C_6D_6$  at 80 °C after complete conversion (121 MHz).



Figure S16. <sup>11</sup>B NMR spectrum  $BH_3$ •THF in THF- $d_8$  (96 MHz).



Figure S17. <sup>11</sup>B NMR spectrum for the addition of 1 eq.of BH<sub>3</sub>•THF to **3a** in THF- $d_8$  (96 MHz).



Figure S18. <sup>31</sup>P NMR spectrum for the addition of 1 eq.of BH<sub>3</sub>•THF to **3a** in THF- $d_8$  (121 MHz).



**Figure S19**. <sup>1</sup>H NMR spectra (300 MHz) for dehydrogenation of **6** by **3a** in THF- $d_8$ : (a) after 1 h at 60 °C, (b) after 3 h at 60 °C, (c) after 24 h at 60 °C).



**Figure S20**. <sup>11</sup>B NMR spectra for dehydrogenation of **6** by **3a** in toluene- $d_8$  resulting in formation of **7**, **8**, **10** and the unknown boron species \* (96 MHz; (a) start at 50 °C, (b) after 60 minutes at 60 °C, (c) after 80 minutes at 60 °C, (d) after 170 minutes at 60 °C, (e) after 1340 minutes at 60 °C). Note that for clarity scaling of spectrum (a) is different than for spectra (b) to (e).