Catalytic Hydrogenation Using Abnormal N-Heterocyclic Carbene Palladium Complexes: Catalytic Scope and Mechanistic Insights

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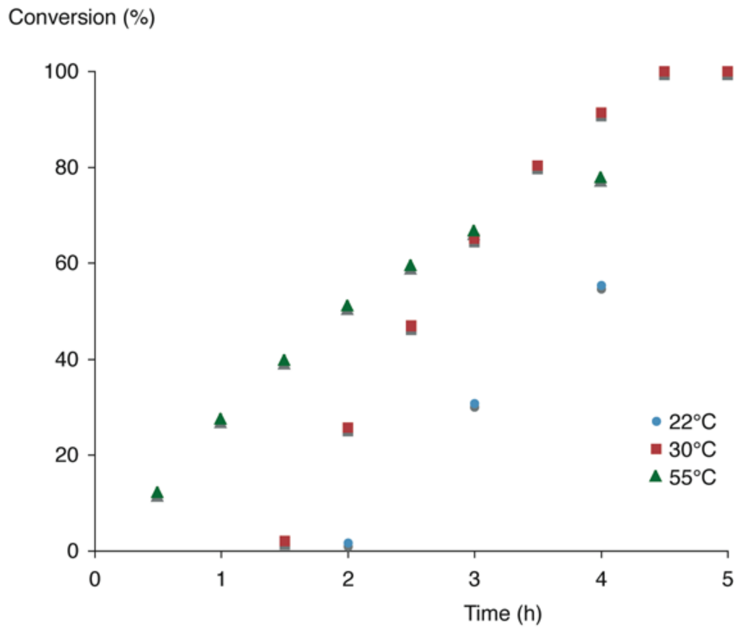
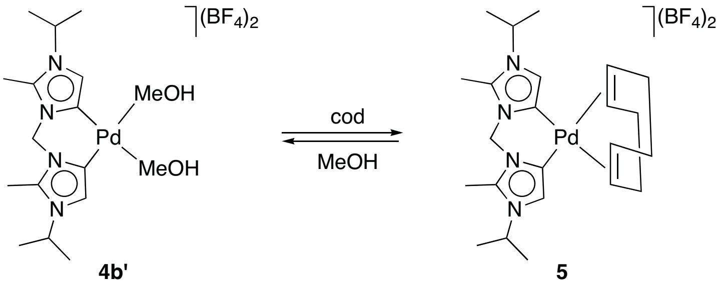


Figure S1. Time-conversion profile for the **4b**-catalyzed cyclooctene hydrogenation at different temperatures.

Table S1. Temperature dependence of the equilibrium constant K.



T	molar fraction **5**	molar fraction **4b'**	K
213	0.760	0.240	13.219
233	0.753	0.247	12.388
253	0.699	0.301	7.702
273	0.720	0.280	9.175
298	0.605	0.395	3.879
312	0.542	0.458	2.589
333	0.450	0.550	1.484

Under the applied conditions (MeOH as solvent), K results from equation 1:

$$K = [\mathbf{5}]\,[\mathbf{4b'}]^{-1}\,[\mathrm{cod}]^{-1} \qquad (1)$$

where [cod] represents the concentration of unbound cyclooctadiene, and [cod] = [**4b'**].

A plot of ln(K) *vs* 1/T is linear within the –60 to 0 °C temperature range (Figure S2) and provides the standard enthalpy and standard entropy for this equilibrium (equation 2):

$$\ln(K) = -\Delta H^\circ R^{-1} T^{-1} + \Delta S^\circ R^{-1} \qquad (2)$$

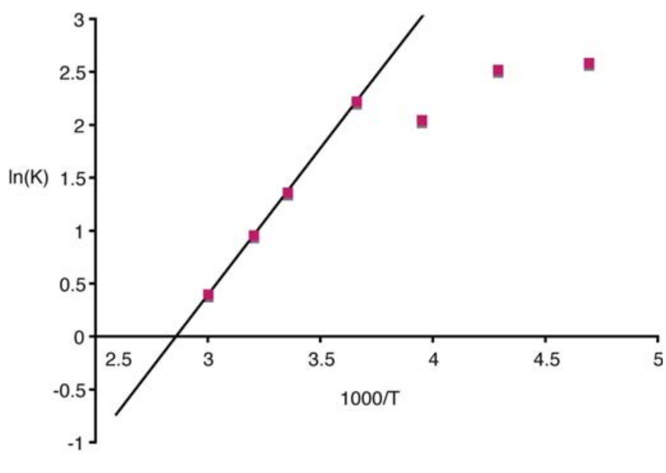


Figure S2. Plot of ln(K) *vs* 1/T.

Table S2. Crystallographic data for complexes **2**, **4a**, **4b**, **4c**, **5**.

	2	**4a**	**4b**	**4c**	**5**
color, shape	colourless block	colourless plate	colourless rod	orange block	colourless rod
crystal size/mm	0.40 × 0.40 × 0.30	0.45 × 0.45 × 0.05	0.45 × 0.30 × 0.20	0.40 × 0.35 × 0.10	0.45 × 0.35 × 0.30
empirical formula	$C_{13}H_{20}B_2F_8N_4Pd$ × 2 CH_3CN	$C_{15}H_{22}B_2F_8N_6Pd$	$C_{19}H_{30}B_2F_8N_6Pd$	$C_{31}H_{38}B_2F_8N_6Pd$ × CH_3CN	$C_{23}H_{36}B_2F_8N_8Pd$
Fw	594.46	566.41	622.51	811.72	648.58
T/K	173(2)	173(2)	173(2)	173(2)	173(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
unit cell					
a/Å	11.4368(11)	12.1881(11)	11.4832(7)	10.6896(5)	11.9038(10)
b/Å	11.4788(10)	12.5443(8)	12.0296(5)	11.2230(6)	21.5551(13)
c/Å	19.375(2)	14.9813(14)	19.3860(12)	31.5382(14)	22.0173(14)
β/deg	103.495(11)	106.608(7)	98.470(5)	94.861(4)	90
V/Å^3	2473.3(4)	2195.0(3)	2648.7(3)	3770.0(3)	5649.4
Z	4	4	4	4	8
D_{calc}/g cm^{-3}	1.596	1.714	1.561	1.430	1.525
μ/mm^{-1} (Mo K_α)	0.827	0.927	0.776	0.565	0.729
no. of total, unique reflns	17458, 4358	41500, 5954	50369, 7185	39767, 6717	42818, 5546
R_{int}	0.1778	0.0658	0.0406	0.0394	0.0970
transmn range	0.174–0.646	0.537–0.947	0.738–0.867	0.782–0.905	0.789–0.816
no. paras, restr.	307, 1	296, 0	314, 16	435, 0	313, 0
R,[a] Rw,[b]	0.0984, 0.2445	0.0624, 0.1616	0.0583, 0.1601	0.0501, 0.1424	0.0692, 0.1751
GOF	1.048	1.038	1.038	1.051	0.899
min, max resid density/e Å^{-3}	–1.446, 1.393	–0.831, 0.0996	–1.628, 1.246	–0.864, 0.977	-1.717, 1.664