Electronic Supplementary Material (ESI) for Dalton Transactions

Catalytic amine-borane dehydrogenation by a PCP-pincer Palladium complex: a combined experimental and DFT analysis of the reaction mechanism.

Andrea Rossin, Giovanni Bottari, Ana M. Lozano-Vila, Margarita Paneque,* Maurizio Peruzzini,* Andrea Rossi, Fabrizio Zanobini.*

Supporting Information

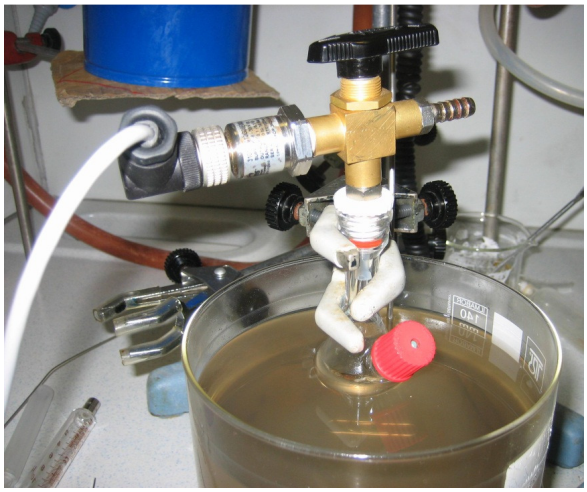


Figure S1. "Man of the moon" device during a catalytic run.

Man of the moon X102 is a device conceived by the University of Zaragoza (Spain) for monitoring the progress of reactions that evolve gases by measuring the pressure variation *vs.* time in closed reaction systems. More information about the features of the kit can be found at the following link: http://www.manonthemoontech.com/x102-gas-evolution.html.

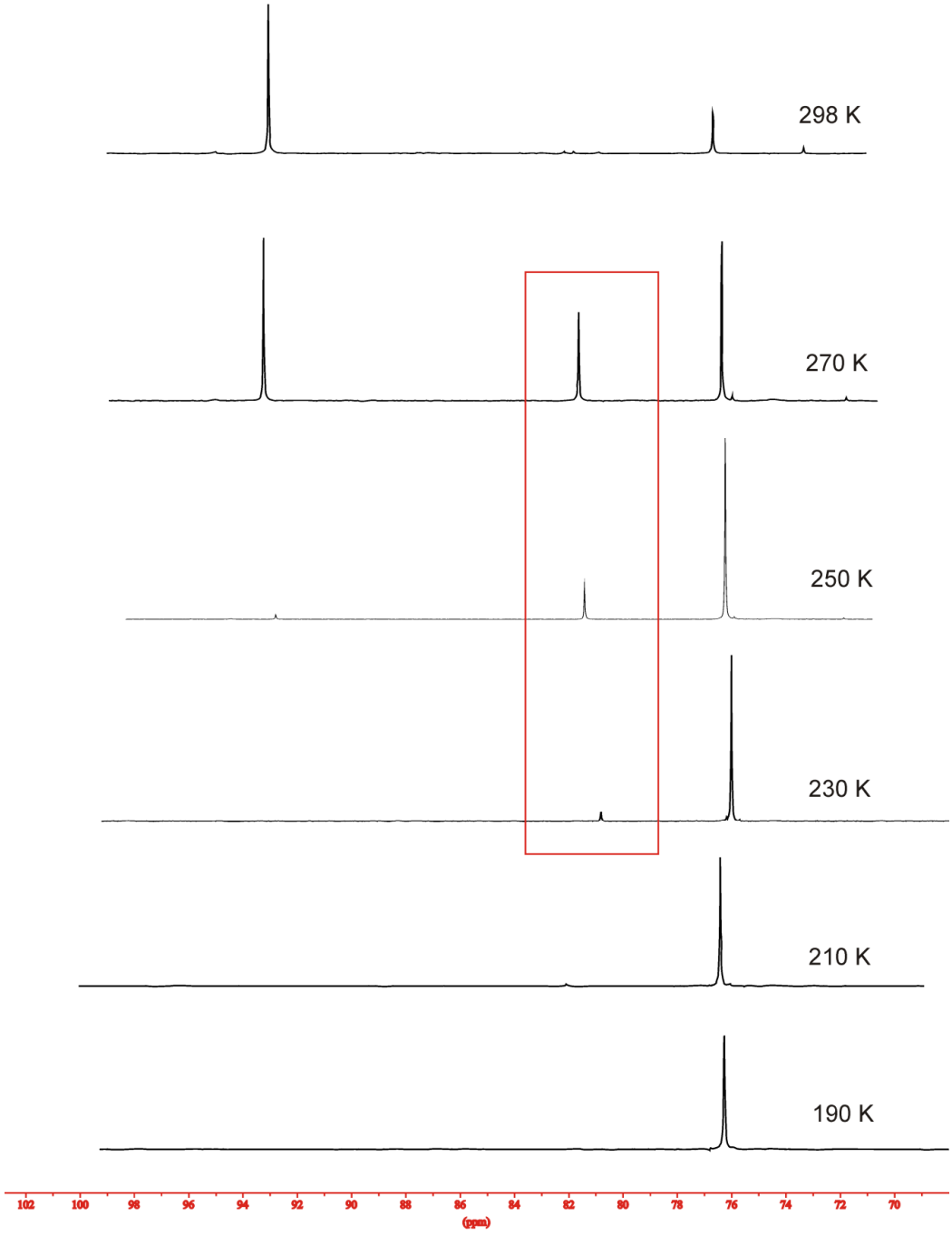


Figure S2. $^{31}P\{^{1}H\}$ VT-NMR spectra of the **2/** $NHMe_2{\cdot}BH_3$ mixture (1:5 stoichiometry, THF-d_8).

The red box highlights the signal of the reaction intermediate detected between 230 and 270 K.

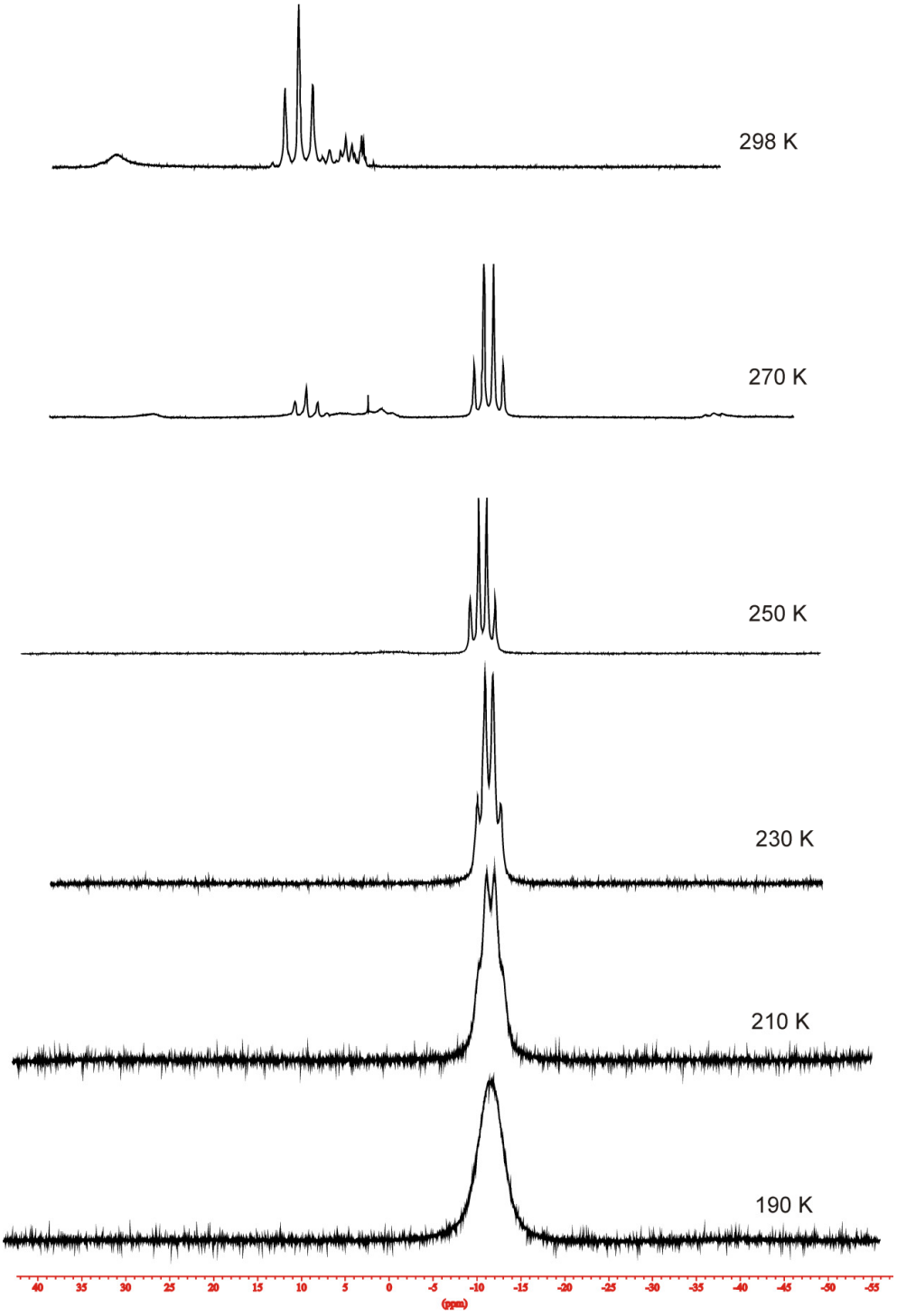


Figure S3. ^{11}B VT-NMR spectra of the **2/** $NHMe_2{\cdot}BH_3$ mixture (1:5 stoichiometry, THF-d_8).

Initial rate experiment on the catalytic dehydrogenation of AB by 2: the evaluation of the reaction order with respect to [AB] was performed through an initial rate experiment at 270 K at two different initial AB concentrations equal to 0.66 and 1.06 M, respectively (determined through ^{11}B NMR signal integration in the presence of an internal $BF_3{\cdot}Et_2O$ standard).[S1] The results are reported on the tables below.

Experiment 1: $[AB]_1 = 0.66$ M

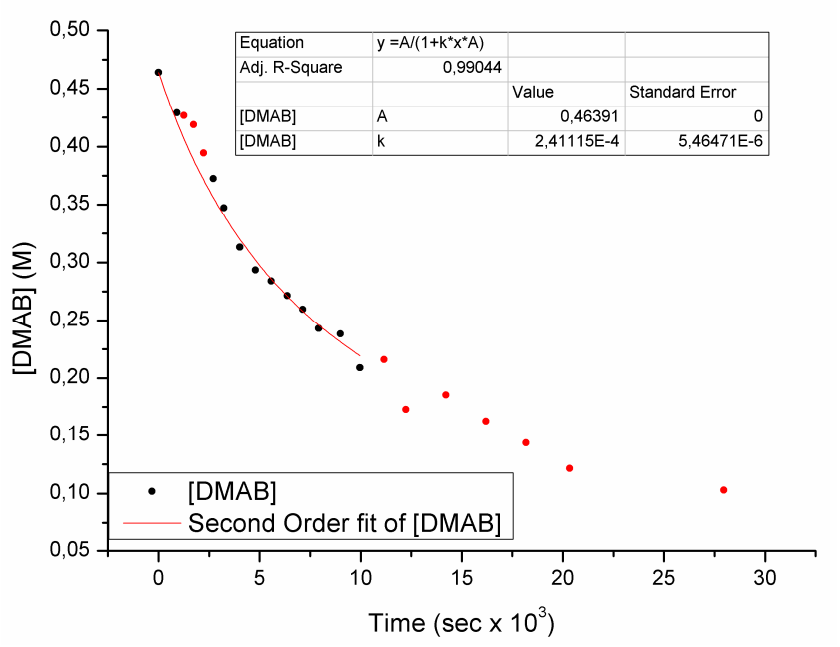
Time (sec)	[AB] (M)
0	0,66
360	0,65
720	0,64
1080	0,63

Experiment 2: $[AB]_2 = 1.06$ M

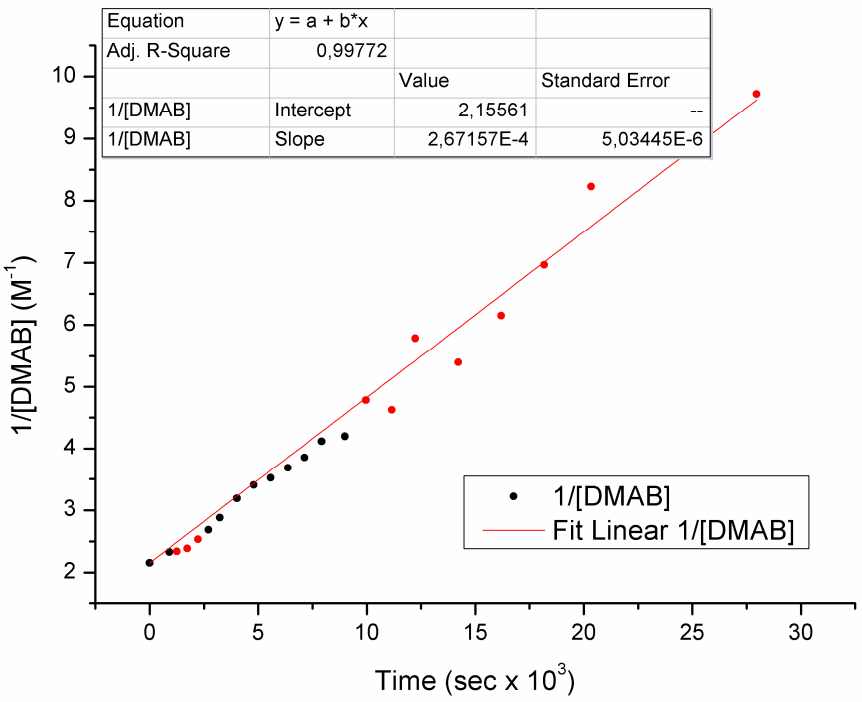
Time (sec)	[AB] (M)
0	1,06
360	1,01
720	0,99
1440	0,97

A mean rate value was calculated from the first collected points, and the results were used in the following equation to infer the reaction order in [AB]:

$$n = \frac{\ln(\bar{v}_1/\bar{v}_2)}{\ln([AB]_1/[AB]_2)} = 2{,}07$$



(a)



(b)

Figure S4. (a) Linear [DMAB] *vs. t* and (b) normalized 1/[DMAB] *vs. t* plots (second order rate law) for the DMAB dehydrogenation reaction catalyzed by **2** (303 K, THF-d_8). The data points depicted in red were excluded from the fitting procedure.

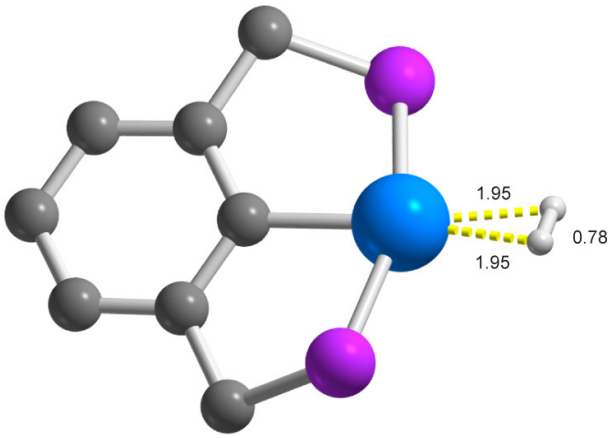


Figure S5. Optimized geometry of $[(^{H}PCP)Pd(\eta^2\text{-}H_2)]^+$. Selected optimized bond lengths reported (Å). H atoms on the pincer ligand omitted for clarity. Atom color code: see Figure 6 in the main text.

Table S1. Crystal data and structure refinement for **2**.

CCDC	891104	
Empirical formula	$C_{24}H_{45}F_6OP_3Pd$	
Formula weight	662.91	
Temperature	120(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	*P* 2_1	
Unit cell dimensions	*a* = 8.501(2) Å	α= 90°.
	b = 16.505(3) Å	β= 106.599(3)°.
	c = 11.134(3) Å	γ = 90°.
Volume	1497.1(8) $Å^3$	
Z	2	
Density (calculated)	1.471 Mg/m^3	
Absorption coefficient	0.833 mm^{-1}	
F(000)	684	
Crystal size	0.15 x 0.17 x 0.2 mm^3	
Theta range for data collection	4.33 to 30.91°.	
Index ranges	$-11 \le h \le 10, -23 \le k \le 19, -15 \le l \le 15$	
Reflections collected	15074	
Independent reflections	7046 [R(int) = 0.0296]	
Completeness to theta = 30.91°	88.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7046 / 1 / 334	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0310, wR2 = 0.0679	
R indices (all data)	R1 = 0.0373, wR2 = 0.0727	
Absolute structure parameter	– 0.093(18)	
Largest diff. peak and hole	0.969 and – 0.474 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1898(4)	6402(2)	3970(3)	14(1)
C(2)	2648(4)	6710(2)	5184(3)	19(1)
C(3)	3932(4)	6279(2)	5999(3)	22(1)
C(4)	4512(4)	5567(2)	5631(3)	25(1)
C(5)	3798(4)	5261(2)	4431(3)	24(1)
C(6)	2485(4)	5667(2)	3611(3)	18(1)
C(7)	1668(4)	5314(2)	2341(3)	20(1)
C(8)	2127(4)	7505(2)	5585(3)	24(1)
C(9)	-1430(5)	7576(2)	5274(3)	25(1)
C(10)	-1345(5)	8097(3)	6434(4)	38(1)
C(11)	-3135(5)	7639(3)	4338(4)	43(1)
C(12)	-1147(6)	6685(2)	5691(4)	38(1)
C(13)	467(5)	8935(2)	4286(3)	26(1)
C(14)	1215(5)	9379(2)	5527(4)	36(1)
C(15)	1656(6)	8993(3)	3486(4)	42(1)
C(16)	-1158(6)	9352(2)	3592(4)	42(1)
C(17)	-1221(4)	5572(2)	217(3)	22(1)
C(18)	-2488(4)	5459(2)	952(4)	31(1)
C(19)	-759(5)	4740(2)	-175(4)	34(1)
C(20)	-2030(4)	6070(2)	-958(3)	29(1)
C(21)	2001(4)	6549(2)	492(3)	25(1)
C(22)	1292(5)	7358(2)	-94(4)	35(1)
C(23)	3624(4)	6734(2)	1497(4)	31(1)
C(24)	2360(5)	5984(3)	-488(3)	34(1)
F(1)	-6712(2)	8538(1)	-1735(2)	26(1)
F(2)	-4728(3)	8748(1)	84(2)	35(1)
F(3)	-4720(3)	7601(1)	-1030(2)	36(1)
F(4)	-2773(2)	8561(1)	-918(2)	30(1)
F(5)	-4759(3)	8363(2)	-2737(2)	38(1)
F(6)	-4778(3)	9497(1)	-1629(2)	37(1)
P(1)	180(1)	7816(1)	4487(1)	17(1)
P(2)	558(1)	6114(1)	1314(1)	15(1)
P(3)	-4755(1)	8551(1)	-1331(1)	19(1)

Pd(1)	60(1)	7020(1)	2753(1)	15(1)
O(1)	-1930(4)	7657(2)	1459(3)	44(1)

Table S3. (Selected) bond lengths [Å] and angles [°] for **2**. Refer to Figure 1 for atom numbering.

C(1)-Pd(1)	2.026(3)
C(7)-P(2)	1.823(3)
C(8)-P(1)	1.828(3)
C(9)-C(11)	1.528(5)
C(9)-P(1)	1.867(4)
C(13)-P(1)	1.884(3)
C(17)-P(2)	1.877(3)
C(21)-P(2)	1.871(3)
F(1)-P(3)	1.595(2)
F(2)-P(3)	1.602(2)
F(3)-P(3)	1.601(2)
F(4)-P(3)	1.615(2)
F(5)-P(3)	1.595(2)
F(6)-P(3)	1.596(2)
P(1)-Pd(1)	2.3138(11)
P(2)-Pd(1)	2.3172(10)
Pd(1)-O(1)	2.157(3)
O(1)-H(1A)	1.00(5)
O(1)-H(1B)	1.07(5)
C(6)-C(1)-Pd(1)	120.7(2)
C(2)-C(1)-Pd(1)	120.6(2)
C(2)-C(8)-P(1)	109.7(2)
C(11)-C(9)-P(1)	110.2(3)
C(10)-C(9)-P(1)	114.2(3)
C(12)-C(9)-P(1)	105.8(3)
C(15)-C(13)-P(1)	105.1(2)
C(14)-C(13)-P(1)	113.3(2)
C(16)-C(13)-P(1)	111.7(3)
C(19)-C(17)-P(2)	112.9(2)
C(20)-C(17)-P(2)	112.5(2)
C(18)-C(17)-P(2)	105.6(2)
C(24)-C(21)-P(2)	114.0(3)
C(22)-C(21)-P(2)	108.0(2)

C(23)-C(21)-P(2)	107.3(2)
C(8)-P(1)-C(9)	105.76(17)
C(8)-P(1)-C(13)	103.41(16)
C(9)-P(1)-C(13)	113.67(16)
C(8)-P(1)-Pd(1)	102.34(11)
C(9)-P(1)-Pd(1)	114.04(12)
C(13)-P(1)-Pd(1)	115.72(11)
C(7)-P(2)-C(21)	106.88(16)
C(7)-P(2)-C(17)	103.86(15)
C(21)-P(2)-C(17)	112.55(16)
C(7)-P(2)-Pd(1)	101.42(10)
C(21)-P(2)-Pd(1)	111.45(12)
C(17)-P(2)-Pd(1)	119.00(11)
F(1)-P(3)-F(5)	90.60(11)
F(1)-P(3)-F(6)	90.25(11)
F(5)-P(3)-F(6)	89.39(14)
F(1)-P(3)-F(3)	90.10(11)
F(5)-P(3)-F(3)	90.57(14)
F(6)-P(3)-F(3)	179.65(12)
F(1)-P(3)-F(2)	90.06(12)
F(5)-P(3)-F(2)	179.17(14)
F(6)-P(3)-F(2)	90.11(13)
F(3)-P(3)-F(2)	89.93(13)
F(1)-P(3)-F(4)	179.79(13)
F(5)-P(3)-F(4)	89.47(11)
F(6)-P(3)-F(4)	89.94(12)
F(3)-P(3)-F(4)	89.71(11)
F(2)-P(3)-F(4)	89.88(12)
C(1)-Pd(1)-O(1)	178.82(13)
C(1)-Pd(1)-P(1)	83.48(9)
O(1)-Pd(1)-P(1)	96.86(9)
C(1)-Pd(1)-P(2)	83.07(9)
O(1)-Pd(1)-P(2)	96.67(9)
P(1)-Pd(1)-P(2)	166.02(3)
Pd(1)-O(1)-H(1A)	121(3)
Pd(1)-O(1)-H(1B)	118(3)
H(1A)-O(1)-H(1B)	101(4)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	14(1)	18(1)	10(1)	0(1)	3(1)	1(1)
C(2)	15(2)	23(1)	17(2)	0(1)	3(1)	2(1)
C(3)	20(2)	24(2)	18(2)	2(1)	-1(1)	2(1)
C(4)	22(2)	26(2)	24(2)	2(1)	0(1)	9(1)
C(5)	24(2)	22(2)	24(2)	4(1)	5(1)	10(1)
C(6)	19(2)	19(2)	17(1)	2(1)	7(1)	2(1)
C(7)	24(2)	18(2)	18(1)	-1(1)	7(1)	2(1)
C(8)	22(2)	24(2)	22(2)	0(1)	-2(1)	6(1)
C(9)	27(2)	28(2)	23(2)	3(1)	13(2)	2(1)
C(10)	45(2)	45(2)	30(2)	-3(2)	19(2)	16(2)
C(11)	26(2)	70(3)	34(2)	2(2)	13(2)	-4(2)
C(12)	51(3)	31(2)	40(2)	5(2)	26(2)	-4(2)
C(13)	38(2)	15(2)	24(2)	0(1)	6(2)	0(1)
C(14)	56(3)	18(2)	28(2)	-3(1)	1(2)	2(2)
C(15)	54(3)	36(2)	36(2)	3(2)	12(2)	-17(2)
C(16)	56(3)	22(2)	35(2)	2(2)	-8(2)	7(2)
C(17)	24(2)	21(2)	22(2)	-3(1)	5(1)	-1(1)
C(18)	24(2)	33(2)	36(2)	-1(2)	6(2)	-10(1)
C(19)	41(2)	27(2)	26(2)	-8(1)	-4(2)	2(2)
C(20)	30(2)	32(2)	21(2)	-3(1)	1(1)	1(2)
C(21)	23(2)	33(2)	22(2)	2(1)	10(2)	-2(1)
C(22)	33(2)	38(2)	38(2)	17(2)	19(2)	-3(2)
C(23)	22(2)	44(2)	28(2)	3(2)	10(2)	-6(1)
C(24)	33(2)	51(2)	24(2)	0(2)	16(2)	4(2)
F(1)	16(1)	33(1)	29(1)	6(1)	5(1)	-1(1)
F(2)	31(1)	51(1)	21(1)	-5(1)	7(1)	6(1)
F(3)	31(1)	23(1)	52(1)	6(1)	11(1)	1(1)
F(4)	15(1)	46(1)	28(1)	1(1)	3(1)	1(1)
F(5)	26(1)	68(2)	20(1)	-5(1)	9(1)	-1(1)
F(6)	27(1)	27(1)	59(2)	10(1)	14(1)	-2(1)
P(1)	20(1)	16(1)	14(1)	-1(1)	3(1)	3(1)
P(2)	17(1)	16(1)	13(1)	0(1)	5(1)	0(1)
P(3)	16(1)	22(1)	19(1)	2(1)	4(1)	0(1)
Pd(1)	15(1)	16(1)	13(1)	0(1)	2(1)	2(1)
O(1)	44(2)	47(2)	33(2)	-5(1)	-3(1)	19(1)

Table S5. Hydrogen bonds for **2**[Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...F(3)	1.00(5)	2.24(5)	3.091(4)	142(4)
O(1)-H(1B)...F(2)	1.07(5)	2.51(5)	3.027(4)	109(3)

Optimized geometries (Cartesian coordinates plus related absolute Gibbs energy in THF).

[(^{H}PCP)Pd(η^1-AB)]$^+$ (2^{H}_AB)

G^{THF} = – 533.856068 ha

C	0.026599	1.711608	-0.022456
C	1.071830	2.352722	0.672738
C	1.027661	3.735294	0.861051
H	1.844894	4.227465	1.387691
C	-0.045239	4.481528	0.393287
H	-0.073224	5.556884	0.553767
C	-1.082921	3.851932	-0.279964
H	-1.928713	4.433850	-0.645727
C	-1.054545	2.474344	-0.504244
C	-2.174326	1.820434	-1.263746
H	-1.959481	1.784071	-2.342035
H	-3.136358	2.330093	-1.134836
C	2.229481	1.563982	1.219336
H	2.028748	1.219720	2.244765
H	3.165952	2.133742	1.240794
P	2.337176	0.055048	0.162585
P	-2.212848	0.071257	-0.669256
Pd	0.085760	-0.325131	-0.349506
H	3.172617	0.413001	-0.926029
H	3.169894	-0.882585	0.827575
H	-3.016995	0.108531	0.499063
H	-3.094186	-0.629336	-1.538421
H	-0.150061	-4.597427	-1.064925
N	-0.070340	-3.892070	-1.797191
B	0.791186	-2.594271	-1.308006
H	-1.013188	-3.656950	-2.104356
H	0.401351	-4.333434	-2.586702
H	0.824455	-1.825606	-2.242338
H	0.147715	-2.205994	-0.293088
H	1.870290	-2.999001	-0.962219

[(^{H}PCP)Pd(σ-*BH*-AB)···AB]$^{+}$ (2^{H}_AB2)

G^{THF} = – 616.977590 ha

C	-0.082014	1.859111	-0.230686
C	0.836827	2.321287	0.732670
C	0.916719	3.687721	1.009561
H	1.636599	4.041012	1.747487
C	0.089728	4.592617	0.358679
H	0.155448	5.653708	0.588528
C	-0.816783	4.141922	-0.591872
H	-1.462545	4.851138	-1.109252
C	-0.905028	2.784589	-0.904308
C	-1.859049	2.325636	-1.972096
H	-1.373133	2.310312	-2.959089
H	-2.751372	2.957186	-2.055397
C	1.745862	1.361852	1.449412
H	1.296546	0.970815	2.374821
H	2.711901	1.807690	1.714670
P	1.920759	-0.068785	0.296620
P	-2.270357	0.571311	-1.560501
Pd	-0.240052	-0.156060	-0.646036
H	2.892305	0.378753	-0.637294
H	2.642052	-1.093843	0.961164
H	-3.405376	0.653721	-0.711466
H	-2.864483	-0.010681	-2.711210
H	1.063043	-3.408428	-0.091330
N	0.654180	-3.695062	-0.987972
B	-0.200194	-2.490962	-1.668905
H	0.056189	-4.494032	-0.779149
H	1.397631	-4.029750	-1.599259
H	-1.060416	-2.961089	-2.364342
H	-0.779485	-1.971694	-0.677157
H	0.567774	-1.776777	-2.278150
H	-1.257399	-0.847773	1.722753
N	-1.214444	-1.510246	2.503577
B	0.263230	-2.237025	2.585913
H	-1.961253	-2.191280	2.377296
H	-1.413237	-0.999750	3.362485
H	0.220640	-3.004385	3.512691
H	0.403222	-2.799037	1.509438

H	1.058566	-1.330848	2.739152

[(^{H}PCP)Pd(σ-*BH*-BH_3-NH_2-BH_2-NH_3)]$^+$ (2^{H}_BNBN)

G^{THF} = – 615.828961 ha

C	-0.042423	2.309438	-0.277594
C	0.871440	2.882213	0.627479
C	1.117311	4.255651	0.586553
H	1.835078	4.691828	1.281055
C	0.450256	5.066987	-0.321508
H	0.642236	6.137485	-0.339261
C	-0.463190	4.509770	-1.206165
H	-0.990182	5.145747	-1.917150
C	-0.710963	3.136084	-1.202119
C	-1.685381	2.545528	-2.182952
H	-1.181311	2.219339	-3.104822
H	-2.482725	3.241156	-2.470067
C	1.575454	2.025568	1.641934
H	0.990048	1.941464	2.569558
H	2.568630	2.404092	1.911305
P	1.641918	0.331560	0.903712
P	-2.328828	1.019889	-1.361022
Pd	-0.389840	0.274404	-0.272170
H	2.840018	0.326733	0.140390
H	2.023233	-0.553798	1.948095
H	-3.410817	1.470819	-0.562080
H	-3.028351	0.266605	-2.341658
N	0.517251	-3.153538	-0.783845
B	-0.690096	-2.146383	-1.070150
H	0.563445	-3.823972	-1.552193
H	1.395945	-2.641176	-0.854999
H	-1.727216	-2.767713	-1.188345
H	-0.840736	-1.499235	0.015145
H	-0.452481	-1.490641	-2.062288
H	-1.667803	-3.763884	0.728512
N	-0.954363	-4.488048	0.839613
B	0.538307	-3.883396	0.614135
H	-1.187522	-5.243137	0.194158

H	-1.024006	-4.866587	1.783448
H	1.304826	-4.810018	0.629154
H	0.706905	-3.062808	1.483204

{(^{H}PCP)Pd[σ-*BH-cyclo*-(BH_2NH_2)$_2$]}$^+$ (2^{H}_cyc)

G^{THF} = – 614.660567 ha

C	-0.090728	2.400672	-0.195630
C	1.039559	2.934885	0.453208
C	1.382808	4.272276	0.248788
H	2.266202	4.676898	0.742068
C	0.607787	5.086655	-0.565605
H	0.879922	6.129586	-0.710641
C	-0.516447	4.567626	-1.193048
H	-1.129453	5.205932	-1.828908
C	-0.870878	3.227762	-1.026300
C	-2.076990	2.679885	-1.735407
H	-1.810731	2.258388	-2.715949
H	-2.859075	3.430740	-1.898279
C	1.875537	2.081233	1.364760
H	1.498222	2.107992	2.397729
H	2.929665	2.381276	1.389249
P	1.647427	0.352949	0.757138
P	-2.652845	1.271637	-0.687678
Pd	-0.594743	0.414699	0.054981
H	2.624957	0.191372	-0.258528
H	2.181466	-0.513478	1.749584
H	-3.488184	1.863697	0.293633
H	-3.624179	0.557997	-1.441664
H	-2.641839	-2.932630	-1.473730
N	-2.226360	-2.979805	-0.549239
B	-0.939655	-2.099036	-0.321553
B	-1.252534	-4.259260	-0.317614
H	-2.968802	-2.907966	0.139805
N	-0.039428	-3.295580	0.172752
H	-1.142429	-1.296216	0.625128
H	-0.530870	-1.634722	-1.358447
H	-0.978339	-4.767087	-1.367252
H	-1.644892	-4.973601	0.559528

H	0.832616	-3.435300	-0.327080
H	0.146552	-3.359607	1.168925

[(^{H}PCP)Pd(η^2-H_2)]$^+$

G^{THF} = – 451.881505 ha

C	0.243693	1.702988	-0.081078
C	1.245649	2.512261	0.485795
C	0.996211	3.873341	0.670292
H	1.776230	4.502942	1.096986
C	-0.229424	4.423930	0.322292
H	-0.413761	5.484022	0.479504
C	-1.219683	3.620980	-0.226434
H	-2.183840	4.050556	-0.496166
C	-0.995887	2.260561	-0.445422
C	-2.072659	1.415192	-1.061824
H	-1.975211	1.373122	-2.156470
H	-3.083327	1.772690	-0.832859
C	2.570171	1.933065	0.890930
H	2.546109	1.555028	1.923422
H	3.393422	2.653544	0.821261
P	2.818762	0.472038	-0.209163
P	-1.770605	-0.292695	-0.430657
Pd	0.592382	-0.302948	-0.377938
H	3.390214	0.989471	-1.398355
H	3.910700	-0.275209	0.303225
H	-2.422193	-0.349682	0.826586
H	-2.578005	-1.182595	-1.185284
H	1.286353	-2.091524	-0.755882
H	0.546073	-2.249385	-0.552485

References

[S1] For further details on this method, see the website:
http://www.chm.davidson.edu/vce/kinetics/MethodOfInitialRates.html