SUPPLEMENTARY INFORMATION

O_2 Insertion into a Palladium-Hydride Bond: Observation of Mechanistic Crossover between HX-Reductive-Elimination and Hydrogen-Atom-Abstraction Pathways

Michael M. Konnick, Nattawan Decharin, Brian V. Popp and Shannon S. Stahl*

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706

Table of Contents **Page**

General Considerations S2

Synthesis and Characterization of Hydrides **1a-1e** S2-S3

Calculated Electronic Effects on the Activation Parameters for H-Atom-Abstraction and HX Reductive Elimination Oxygenation Mechanisms S4-S5

Full *Gaussian 03* Reference S6

Total Energies, Thermochemical Analysis, and Three Lowest Frequencies from Normal Mode Analysis S7

Cartesian Coordinates for Optimized Complexes S8-S16

X-Ray Crystallographic Data for Compound **1d** S17-S32

General Considerations

All procedures, except the oxygenation reactions, were carried out under an inert atmosphere of nitrogen in a MBraun glove box or by using standard Schlenk techniques. The benzoic acids, 1,3,5-trimethoxybenzene, and oxygen gas were used without purification. *p*-Methoxybenzoic acid-*d* was prepared by dissolving *para*-methoxybenzoic acid in methanol-d_4 and then evaporating the methanol-d_4 six times. All solvents used were dried and deoxygenated prior to usage: diethyl ether, pentane, and toluene were passed through a column of activated alumina and Q4. C_6D_6 was degassed via standard freeze/pump/thaw methods and then dried by distillation from Na/benzophenone. NMR data were recorded using a Varian Inova (^{1}H: 500 MHz or ^{1}H: 600MHz) spectrometer. Spectra recorded at elevated temperatures were calibrated with ethylene glycol. Elevated pressures of O_2 were achieved by condensing oxygen into an NMR tube by cooling the tube with liquid N_2.

Synthesis and Characterization of Compounds

The synthesis of the new hydride compounds follows the established literature procedure[1] which proceeds as follows: $Pd(IMes)_2$ (52.0 mg, 72.7μmol) was dissolved in 10 mL of diethyl ether. A solution of benzoic acid (8.9mg, 72.9μmol) in diethyl ether (10 mL) was added dropwise over the course of 5 minutes. After allowing the solution to stir for 48 hours, a faint yellow color (associated with trace $Pd(IMes)_2$) was evident, indicating that no unreacted acid remained in solution. The solution was filtered through celite and evaporated. Recrystallization from ether/pentane at -30°C yielded the colorless **1a**.

1a$^{(H)}$: Yield: 39 mg (64%). ^{1}H NMR (500 MHz, C_6D_6): d 8.09 (*o*-benzoate, m, 2H), 7.33 (*m*-benzoate, m, 2H), 7.28 (*p*-benzoate, m, 1H), 6.80 (IMes aryl, s, 8H), 6.10 (IMes olefin, s, 4H), 2.34 (*p*-Me, s, 12H), 2.00 (*o*-Me, s, 24H), -17.82 (Pd-H, s, 1H); ^{13}C NMR (125 MHz, C_6D_6): d 186.0 (N-**C**-N), 169.2 (Ar-**C**OO-), 141.4, 137.7, 137.4, 136.4, 131.0, 129.4, 128.7, 127.0 (aryl C), 121.2 (-H**C**=**C**H-), 21.7 (*p*-Me), 18.8 (*o*-Me); MS (ESI-TOF): 715.3 $[M\text{-}PhCO_2]^+$. Anal. Calcd for $C_{49}H_{54}N_4O_2Pd$: C, 70.28; H, 6.50; N, 6.69. Found: C, 70.06; H, 6.54; N, 6.58.

1b$^{(NO2)}$: Yield: 56 mg (72%). ^{1}H NMR (500 MHz, C_6D_6): d 8.08 (*o*-benzoate, dd, 2H), 7.88 (*m*-benzoate, dd, 2H), 6.75 (IMes aryl, s, 8H), 6.16 (IMes olefin, s, 4H), 2.31 (*p*-Me, s, 12H), 1.92 (*o*-Me, s, 24H), -18.02 (Pd-H, s, 1H); ^{13}C NMR (125 MHz, C_6D_6): d 185.1 (N-**C**-N), 167.2 (Ar-**C**OO-), 149.0, 146.4, 137.7, 137.5, 136.2, 131.3, 129.4, 122.4 (aryl C), 121.4 (-H**C**=**C**H-), 21.6 (*p*-Me), 18.6 (*o*-Me); MS (ESI-TOF): 715.3 $[M\text{-}(O_2N)ArCO_2]^+$. Anal. Calcd for $C_{49}H_{53}N_5O_4Pd$: C, 66.70; H, 6.05; N, 7.94. Found: C, 66.48; H, 6.02; N, 7.75.

1c$^{(Cl)}$: Yield: 28 mg (54%). ^{1}H NMR (500 MHz, C_6D_6): d 7.89 (*o*-benzoate, dd, 2H), 7.29 (*m*-benzoate, dd, 2H), 6.77 (IMes aryl, s, 8H), 6.08 (IMes olefin, s, 4H), 2.32 (*p*-Me, s, 12H), 1.96 (*o*-Me, s, 24H), -17.86 (Pd-H, s, 1H); ^{13}C NMR (125 MHz, C_6D_6): d 185.6 (N-**C**-N), 168.1 (Ar-**C**OO-), 139.8, 137.6, 137.5, 136.4, 134.7, 132.5, 129.4, 127.2 (aryl C), 121.3 (-H**C**=**C**H-), 21.7 (*p*-Me), 18.7 (*o*-Me). Anal. Calcd for $C_{49}H_{53}ClN_4O_2Pd$: C, 67.50; H, 6.13; N, 6.43. Found: C, 67.22; H, 6.18; N, 6.21.

1d$^{(Me)}$: Yield: 35 mg (55%). ^{1}H NMR (500 MHz, C_6D_6): d 8.01 (*o*-benzoate, dd, 2H), 7.13 (*m*-benzoate, dd, 2H), 6.82 (IMes aryl, s, 8H), 6.10 (IMes olefin, s, 4H), 2.35 (*p*-Me, s, 12H), 2.25 (benzoate-Me, s, 3H) 2.00 (*o*-Me, s, 24H), -17.79 (Pd-H, s, 1H); ^{13}C NMR (125 MHz, C_6D_6): d 185.9 (N-**C**-N), 169.7 (Ar-**C**OO-), 138.5, 137.9, 137.7, 137.5, 136.5, 131.1, 129.4, 127.9 (aryl C), 121.3 (-H**C**=**C**H-), 21.8 (*p*-**Me**ArCOO-), 21.7 (*p*-Me), 18.7 (*o*-Me). X-Ray: (see data and

tables below). Anal. Calcd for $C_{50}H_{56}N_4O_2Pd$: C, 70.53; H, 6.63; N, 6.58. Found: C, 69.71; H, 6.65; N, 6.39.

1e$^{(OMe)}$: Yield: 48 mg (65%). ^{1}H NMR (500 MHz, C_6D_6): d 8.04 (*o*-benzoate, dd, 2H), 6.91 (*m*-benzoate, dd, 2H), 6.81 (IMes aryl, s, 8H), 6.10 (IMes olefin, s, 4H), 3.41 (benzoate-OMe, s, 3H), 2.34 (*p*-Me, s, 12H), 2.02 (*o*-Me, s, 24H), -17.71 (Pd-H, s, 1H); ^{13}C NMR (125 MHz, C_6D_6): d 186.1 (N-**C**-N), 169.2 (Ar-**C**OO-), 160.8, 137.7, 137.4, 136.5, 134.4, 132.4, 129.4, (aryl C), 121.2 (-H**C**=**C**H-), 112.3 (aryl C), 55.0 (O**C**H$_3$), 21.7 (*p*-Me), 18.8 (*o*-Me); MS (ESI-TOF): 715.3 [M-(MeO)ArCO$_2$]$^+$. Anal. Calcd for $C_{50}H_{56}ClN_4O_3Pd$: C, 69.23; H, 6.51; N, 6.46. Found: C, 69.51; H, 6.79; N, 6.23.

Calculated Electronic Effects on the Activation Parameters for H-Atom-Abstraction and HX-Reductive-Elimination Oxygenation Mechanisms

The calculated free energies of activation were plotted with respect to Hammett σ_p parameters to examine the electronic effect of the benzoate *para*-substituent on the H-atom-abstraction (HAA) and HX-reductive-elimination (HXRE) mechanisms (Fig. S1; cf. Fig. 5 reproduced from the manuscript below). The significant scatter present in the data in Fig. S1 largely reflects scatter introduced by the calculated entropies of activation, $\Delta S^{\ddagger}$ (Fig. S2). As shown in Figures S3 - S4, much less scatter is evident in Hammett plots based on the calculated electronic energies and enthalpies of activation, $\Delta E^{\ddagger}$ (Fig. S3) and $\Delta H^{\ddagger}$ (Fig. S4). The scatter in the calculated entropy introduced by the *para* substituents is present for *both* the HXRE and HAA mechanisms. Thus, the scatter is eliminated when the Hammett plot is based on the *relative* free energies of activation (i.e., $\Delta\Delta G^{\ddagger}_{calc}$; see Fig. 5 from the manuscript below)

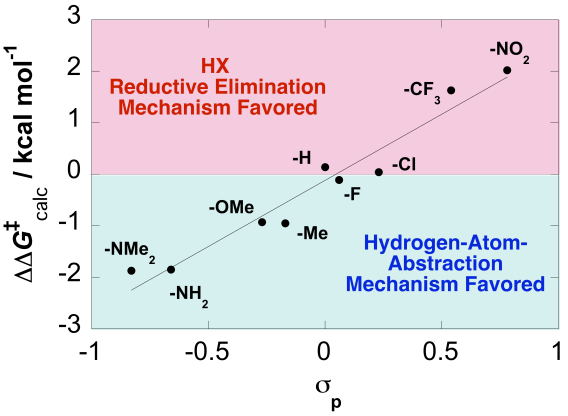

Fig. 5 (reproduced from manuscript): Hammett plot of the relative calculated free-energies of activation ($\Delta\Delta G^{\ddagger}_{calc} = \Delta G^{\ddagger}_{HAA} - \Delta G^{\ddagger}_{HXRE}$) for the hydrogen-atom-abstraction (HAA) and HX-reductive-elimination (HXRE) pathways for O_2 insertion into the Pd^{II}–H bond of $(IMe)_2Pd(H)(O_2CC_6H_4X)$.

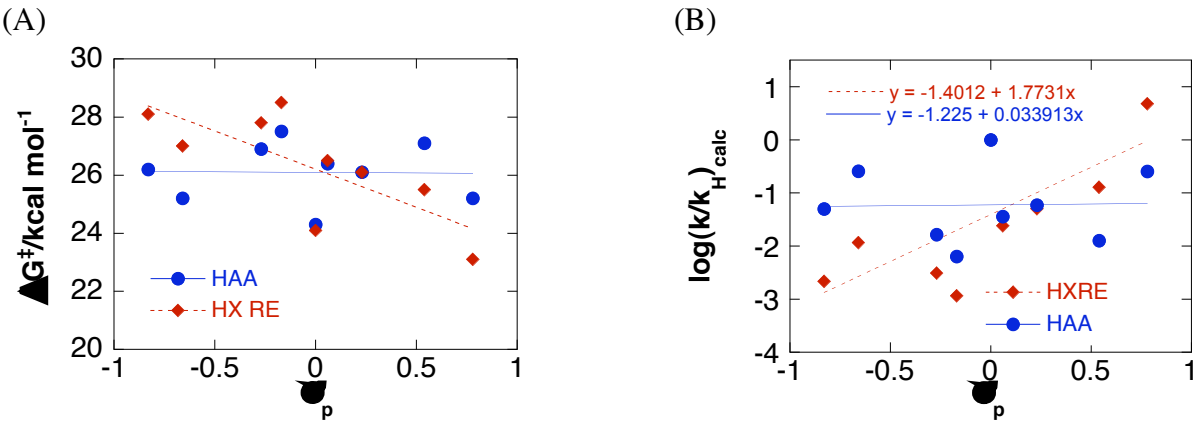

Fig. S1. (A) Correlation between the calculated free energies of activation for HAA and HXRE mechanism with respect to the Hammett parameter σ_p (B) Calculated Hammett plot based on the calculated rate constants for the reaction of $(IMe)_2Pd(H)(O_2CC_6H_4X)$ complexes with O_2.

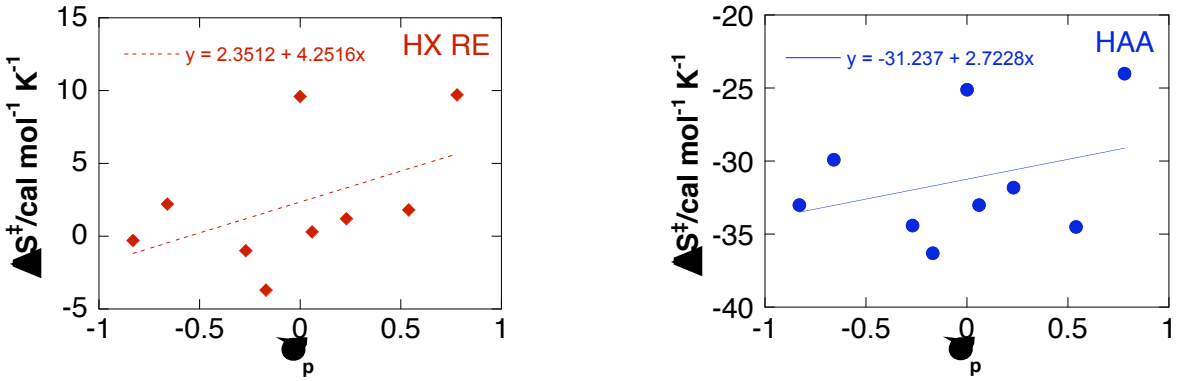

Fig. S2. Correlation between the calculated entropy of activation for HAA and HXRE mechanism with the sigma parameter

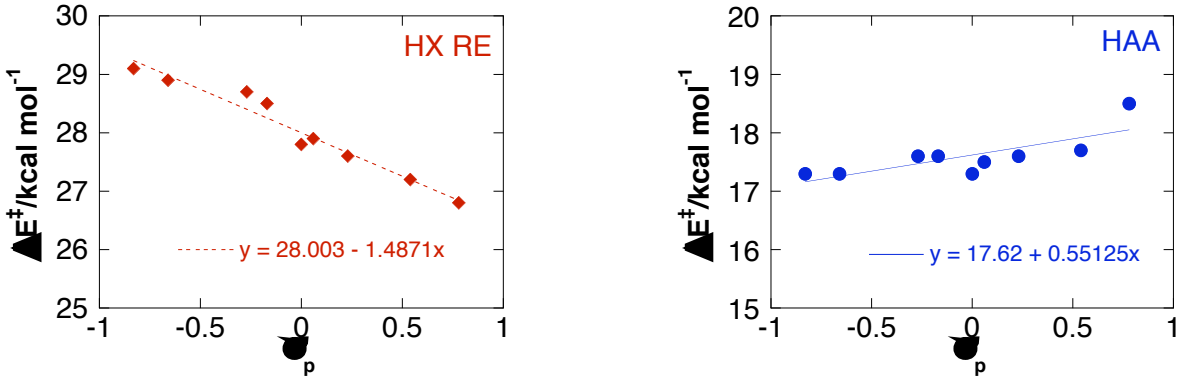

Fig. S3. Correlation between the calculated total energy of activation for HAA and HXRE mechanism with the sigma parameter

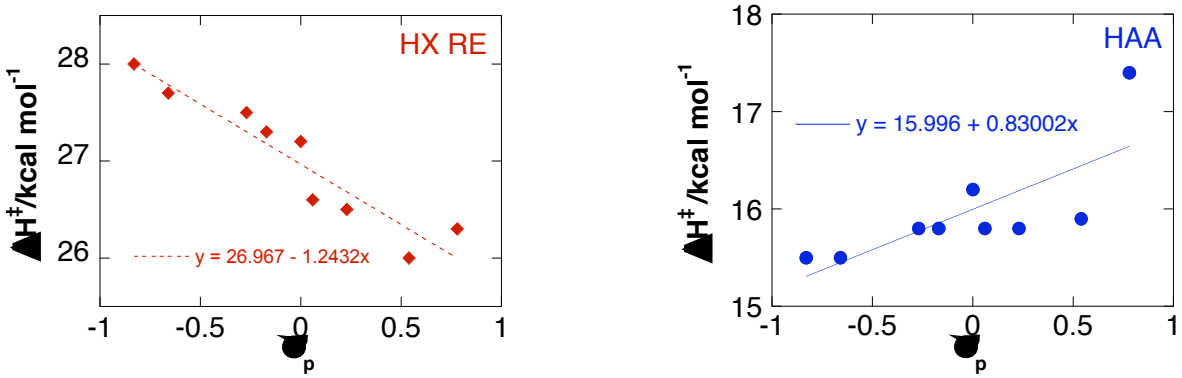

Fig. S4. Correlation between the calculated enthalpy of activation for HAA and HXRE mechanism with the sigma parameter

Full *Gaussian 03* Reference

Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Solvation-Corrected Energies and Thermochemical Corrections at 323.15 K (kcal/mol) and Three Lowest Frequencies from Normal-Mode Analysis

Label		E_{sol}	s^2	G_{sol}	H	S	ΔG	ΔE	ΔH	ΔS	Frequencies (cm^{-1})
O_2	Triplet O_2	-94356.53	2.0089	-94370.06	-94351.93	56.09					1641.60
-NMe_2	Pd(IMe)$_2$(H)(*p*-NMe_2-	-811197.83	0.0000	-810968.03	-810896.45	221.50					4.45, 15.63, 25.68
-NMe_2	HAA TS	-905537.06	2.0132	-905311.89	-905232.85	244.57	26.21	17.30	15.54	-33.02	-1528.28,11.21,14.65
-NMe_2 RE^{TS}	RE TS	-811168.68	0.0000	-810939.95	-810868.48	221.17	28.08	29.15	27.97	-0.33	-411.08, 7.72, 16.64
-NH_2	Pd(IMe)$_2$(H)(*p*-NH_2-OBz)	-761861.50	0.0000	-761663.51	-761597.70	203.66					11.13, 18.57, 28.44
-NH_2 HAA^{TS}	HAA TS	-856200.70	2.0133	-856008.42	-855934.13	229.89	25.15	17.33	15.50	-29.86	-1534.34, 10.52,14.18
-NH_2 RE^{TS}	RE TS	-761832.56	0.0000	-761636.51	-761569.99	205.84	27.00	28.94	27.71	2.18	-411.04, 10.00, 15.13
-OMe	Pd(IMe)$_2$(H)(*p*-OMe-OBz)	-798996.49	0.0000	-798790.99	-798721.85	213.96					6.32,13.71,25.13
-OMe	HAA TS	-893335.46	2.0133	-893134.14	-893057.99	235.64	26.92	17.55	15.80	-34.41	-1534.04,11.95,16.35
-OMe RE^{TS}	RE TS	-798967.79	0.0000	-798763.15	-798694.32	212.98	27.85	28.69	27.53	-0.97	-391.34,7.42,17.46
-Me	Pd(IMe)$_2$(H)(*p*-Me-OBz)	-751788.94	0.0000	-751587.08	-751518.11	213.44					4.90,8.47,17.34
-Me HAA^{TS}	HAA TS	-846127.91	2.0133	-845929.62	-845854.25	233.20	27.53	17.56	15.79	-36.33	-1538.32,12.57,13.60
-Me RE^{TS}	RE TS	-751760.45	0.0000	-751558.60	-751490.83	209.72	28.48	28.50	27.27	-3.73	-396.60,9.91,15.04
-H	Pd(IMe)$_2$(H)(*p*-H-OBz)	-727111.41	0.0000	-726921.42	-726859.75	190.85					4.90,8.47,17.34
-H HAA^{TS}	HAA TS	-821450.68	2.0134	-821267.20	-821195.52	221.82	24.28	17.26	16.16	-25.12	-1538.32,12.57,13.59
-H RE^{TS}	RE TS	-727083.59	0.0000	-726897.28	-726832.52	200.41	24.14	27.82	27.23	9.56	-396.60,9.91,15.04
-F	Pd(IMe)$_2$(H)(*p*-F-OBz)	-789405.01	0.0000	-789223.20	-789157.27	204.01					7.00,14.78,26.96
-F HAA^{TS}	HAA TS	-883744.02	2.0134	-883566.84	-883493.44	227.15	26.42	17.52	15.77	-32.96	-1545.88,7.19,17.10
-F RE^{TS}	RE TS	-789377.15	0.0000	-789196.67	-789130.64	204.34	26.53	27.85	26.63	0.32	-375.98,9.32,14.42
-Cl	Pd(IMe)$_2$(H)(*p*-Cl-OBz)	-1015530.79	0.0000	-1015350.22	-1015283.66	205.98					10.19,15.57,25.95
-Cl HAA^{TS}	HAA TS	-1109869.71	2.0134	-1109694.19	-1109619.77	230.28	26.10	17.61	15.82	-31.79	-1542.96,11.88,14.23
-Cl RE^{TS}	RE TS	-1015503.16	0.0000	-1015324.17	-1015257.20	207.22	26.06	27.63	26.46	1.24	-375.98,8.39,15.74
-CF_3	Pd(IMe)$_2$(H)(*p*-CF_3-OBz)	-938676.74	0.0000	-938490.45	-938419.03	221.01					8.05,12.89,16.49
-CF_3 HAA^{TS}	HAA TS	-1033015.56	2.0135	-1032833.42	-1032755.04	242.55	27.09	17.71	15.92	-34.55	-1544.86,10.33,13.41
-CF_3 RE^{TS}	RE TS	-938649.52	0.0000	-938464.99	-938392.99	222.82	25.46	27.22	26.04	1.81	-340.23, 7.98, 10.76
-NO_2	Pd(IMe)$_2$(H)(*p*-NO_2-OBz)	-855479.93	0.0000	-855291.35	-855224.90	205.66					-4.49,14.76,24.93
-NO_2 HAA^{TS}	HAA TS	-949817.93	2.0136	-949636.26	-949559.44	237.72	25.16	18.53	17.39	-24.03	-1549.87,11.72,14.68
-NO_2 RE^{TS}	RE TS	-855453.17	0.0000	-855268.22	-855198.61	215.39	23.14	26.76	26.28	9.73	-320.52,9.09,14.69

-NMe_2

N	-2.667089	-2.871964	1.008636
C	-2.289217	-2.011690	0.020228
N	-2.019874	-2.818399	-1.043066
C	-2.226747	-4.152931	-0.725348
C	-2.629476	-4.189658	0.571977
Pd	-2.122547	0.027024	0.095769
C	-2.107832	2.072421	0.083078
N	-2.155282	2.936510	1.135826
C	-2.081017	4.255741	0.707963
C	-1.989297	4.214907	-0.647583
N	-2.005601	2.876400	-1.009771
C	-2.226113	2.529073	2.532221
C	-1.916932	2.377435	-2.383487
C	-1.619867	-2.337631	-2.366468
C	-3.012858	-2.465291	2.363720
O	0.032593	-0.053520	0.374333
C	0.804930	0.054363	-0.648024
O	0.423151	0.167267	-1.838593
C	2.283713	0.031920	-0.351454
C	3.219037	0.141672	-1.388700
C	4.589535	0.115352	-1.141846
C	5.090889	-0.014659	0.175840
C	4.142013	-0.140590	1.219087
C	2.774852	-0.111783	0.953020
N	6.463293	-0.004414	0.437323
H	-3.679904	0.096524	-0.008103
H	-2.892702	2.003000	-2.708457
H	-1.609581	3.202121	-3.031854
H	-1.905770	5.008294	-1.374843
H	-2.090175	5.089379	1.393875
H	-2.879919	-5.020632	1.214135
H	-2.066512	-4.946947	-1.439047
H	-1.172385	1.576735	-2.422186
H	-1.313074	2.821444	3.061278
H	-3.094037	2.988805	3.017009
H	-2.323536	1.442971	2.557587
H	-3.205025	-1.391437	2.351971
H	-3.911946	-2.996513	2.691902
H	-2.189224	-2.679506	3.053518
H	-2.506521	-2.146891	-2.981146
H	-1.033409	-1.420923	-2.256948
H	-1.003987	-3.103264	-2.846496
H	2.851976	0.243232	-2.405692
H	5.268223	0.198031	-1.983045
H	4.466870	-0.261368	2.246303
H	2.063800	-0.209211	1.767637
C	6.930730	-0.426115	1.748273
C	7.390359	-0.160578	-0.672469
H	8.413215	-0.106747	-0.291854
H	7.266493	-1.120315	-1.203730
H	7.268627	0.649099	-1.400564
H	8.019132	-0.335970	1.784273
H	6.522247	0.218150	2.534819
H	6.659995	-1.469831	1.985544

-NMe_2 HAA^{TS}

N	1.886109	-2.752795	-1.018941
C	2.146350	-1.898552	0.010164
N	2.692042	-2.691400	0.976113
C	2.774931	-4.010797	0.557459
C	2.268258	-4.047704	-0.703211
Pd	1.772485	0.125002	0.076525
C	1.558323	2.169926	0.063637
N	1.433596	2.972916	-1.028399
C	1.252963	4.296597	-0.659407
C	1.260848	4.329299	0.699930
N	1.447232	3.020651	1.122782
C	1.456900	2.481429	-2.407549
C	1.493657	2.607274	2.519520
C	3.141272	-2.218082	2.279042
C	1.329082	-2.354904	-2.312312
O	-0.379688	-0.139365	0.473689
C	-1.137113	-0.040815	-0.563347
O	-0.733754	0.131675	-1.738374
C	-2.616782	-0.155974	-0.301273
C	-3.532989	-0.037753	-1.355026
C	-4.905140	-0.140832	-1.143300
C	-5.426797	-0.383924	0.150856
C	-4.497739	-0.485997	1.214856
C	-3.128443	-0.378113	0.984485
N	-6.796704	-0.531468	0.365775
O	4.746746	0.526222	-0.197299
O	5.410661	-0.487577	0.227858
H	3.514235	0.326452	-0.094300
H	0.601879	2.963166	3.044617
H	2.390068	3.004743	3.007842
H	1.513235	1.517117	2.546752
H	1.144041	5.151169	1.390121
H	1.127307	5.086105	-1.384785
H	1.124110	3.286078	-3.068042
H	2.473570	2.184656	-2.682884
H	0.777096	1.628928	-2.487304
H	0.746289	-1.438315	-2.188612
H	2.135920	-2.194181	-3.036043
H	2.143115	-4.869835	-1.391706
H	0.671281	-3.149906	-2.675103
H	2.573147	-2.708142	3.076723
H	2.971967	-1.141210	2.320647
H	4.209354	-2.418467	2.404880
H	3.175284	-4.793596	1.183996
H	-3.149502	0.142455	-2.354820
H	-5.569997	-0.034150	-1.992856
H	-4.840820	-0.653589	2.229380
H	-2.433641	-0.464866	1.814146
C	-7.303835	-0.524427	1.728454
C	-7.722045	-0.161583	-0.693362
H	-8.385294	-0.678267	1.706951
H	-6.867090	-1.342411	2.312818
H	-7.098213	0.421958	2.257928
H	-8.743086	-0.363026	-0.360997
H	-7.650817	0.904041	-0.971291
H	-7.545611	-0.760379	-1.594196

-NMe_2 RE^{TS}

N	0.399446	2.535579	1.234589
C	1.081918	2.092152	0.141894
N	0.568900	2.809550	-0.892979
C	-0.429886	3.666938	-0.458728
C	-0.536134	3.495448	0.886087
Pd	2.382141	0.498155	0.159687
C	3.610817	-1.141926	0.021099
N	4.957041	-1.178438	-0.216432
C	5.420212	-2.483569	-0.274186
C	4.339190	-3.284556	-0.072446
N	3.247612	-2.452074	0.106394
C	5.798517	-0.000452	-0.389200
C	1.876895	-2.933989	0.313507
C	0.875214	2.560773	-2.300009
C	0.520148	1.923175	2.556463
O	-0.302311	-0.691291	0.886371
C	-0.919314	-0.580221	-0.223279
O	-0.390911	-0.392861	-1.355453
C	-2.437851	-0.684342	-0.174486
C	-3.210001	-0.564921	-1.337093
C	-4.600859	-0.654652	-1.307539
C	-5.290596	-0.886161	-0.093832
C	-4.509738	-0.993750	1.081183
C	-3.119085	-0.900004	1.029917
N	-6.684680	-1.024961	-0.060876
H	1.997646	0.237055	-1.278030
H	0.205466	0.876709	2.482732
H	1.553830	1.993546	2.910799
H	-1.187345	3.959791	1.610834
H	-0.973883	4.308604	-1.134729
H	6.458312	-2.723922	-0.448692
H	4.252802	-4.360418	-0.042799
H	-0.124384	2.462306	3.254917
H	0.496807	3.396868	-2.893832
H	1.956499	2.484367	-2.428628
H	0.398323	1.624794	-2.606496
H	5.145108	0.873633	-0.422387
H	6.501215	0.096364	0.445594
H	6.357922	-0.074460	-1.327306
H	1.865698	-3.630529	1.157827
H	1.214878	-2.085671	0.520593
H	1.529558	-3.444958	-0.589711
H	-2.696339	-0.397644	-2.279437
H	-5.146085	-0.550700	-2.239103
H	-4.982466	-1.159306	2.043054
H	-2.535621	-0.995865	1.941153
C	-7.360216	-0.960826	1.224579
C	-7.454133	-0.601958	-1.219696
H	-8.513647	-0.795308	-1.033264
H	-7.331309	0.471300	-1.450661
H	-7.168431	-1.174726	-2.108746
H	-8.432190	-1.109626	1.071535
H	-7.010870	-1.758632	1.889114
H	-7.213037	0.003946	1.742445

-NH_2

C	0.042784	0.231459	0.123103
C	-0.085811	-0.081860	1.483791
C	1.085407	-0.254914	2.236537
C	2.343386	-0.119812	1.653099
C	2.467252	0.194428	0.287465
C	1.295693	0.369070	-0.470522
C	-1.454760	-0.219918	2.105206
O	-2.468895	-0.052302	1.384933
O	-1.470643	-0.506974	3.357994
Pd	-3.383555	-0.563960	4.392766
C	-3.383701	1.468831	4.625461
N	-2.804353	2.215028	5.607608
C	-2.993975	3.572960	5.386469
C	-3.714034	3.677859	4.238372
N	-3.940382	2.385678	3.788388
C	-2.045032	1.662520	6.720857
C	-4.679380	2.039334	2.572869
C	-3.555269	-2.593176	4.184937
N	-3.950689	-3.274561	3.074210
C	-3.929097	-4.644493	3.291939
C	-3.502837	-4.832448	4.568450
N	-3.285431	-3.567935	5.099714
C	-4.396240	-2.644650	1.830410
C	-2.781133	-3.316839	6.442865
H	-4.708225	-0.599411	5.219708
H	-5.667301	1.647198	2.834558
H	-4.795564	2.943260	1.969340
H	-4.071940	4.545481	3.705009
H	-2.598474	4.329117	6.047775
H	-3.330271	-5.736166	5.133321
H	-4.211042	-5.353826	2.528473
H	-4.111342	1.290444	2.013381
H	-0.993723	1.960511	6.650537
H	-2.461980	2.009892	7.672205
H	-2.115021	0.575517	6.663909
H	-2.980086	-2.272062	6.686096
H	-3.296495	-3.965726	7.157991
H	-1.702615	-3.502508	6.492590
H	-5.477082	-2.468356	1.863828
H	-3.864735	-1.698629	1.693488
H	-4.163605	-3.312231	0.996000
H	-0.861718	0.364970	-0.462551
H	1.372575	0.619311	-1.527566
H	3.240773	-0.251892	2.255874
H	0.993383	-0.499788	3.290035
N	3.730852	0.389306	-0.290809
H	4.492953	-0.091622	0.172762
H	3.767476	0.255512	-1.294670

-NH_2 HAA^{TS}

C	3.416700	-0.311766	-0.879429
C	2.870126	-0.157969	0.403195
C	3.747701	-0.117384	1.497030
C	5.125001	-0.228219	1.319463
C	5.668788	-0.383964	0.031434
C	4.791951	-0.423885	-1.067965
C	1.376155	-0.042501	0.579481
O	0.636789	-0.073482	-0.432984
O	0.969563	0.085665	1.793958
Pd	-1.217569	0.159525	2.053140
C	-1.341722	-1.893352	1.997839
N	-1.619864	-2.668184	0.913624
C	-1.578810	-4.015567	1.236371
C	-1.261382	-4.093189	2.556231
N	-1.120303	-2.786898	3.003302
C	-1.913026	-2.134091	-0.417846
C	-0.754633	-2.420556	4.365446
C	-1.284042	2.217096	2.079542
N	-1.356411	3.050816	3.155860
C	-1.383323	4.380279	2.762224
C	-1.323830	4.381362	1.404309
N	-1.259179	3.055089	1.005592
C	-1.424526	2.607779	4.542368
C	-1.224046	2.617311	-0.390439
O	-4.162035	0.224464	2.690711
O	-4.498421	1.307465	3.292779
H	-2.940698	0.230987	2.411555
H	0.195068	-2.890777	4.639278
H	-1.535098	-2.732374	5.067793
H	-0.640751	-1.336336	4.402228
H	-1.118038	-4.946292	3.202145
H	-1.767246	-4.789679	0.507949
H	-1.803180	-2.940480	-1.147469
H	-2.937892	-1.750981	-0.453320
H	-1.198670	-1.336881	-0.640113
H	-0.721537	1.648279	-0.452124
H	-2.242651	2.541088	-0.786803
H	-1.314060	5.197072	0.697165
H	-0.662265	3.350131	-0.976468
H	-0.617222	3.065121	5.123448
H	-1.310563	1.522949	4.553533
H	-2.393333	2.871915	4.977112
H	-1.434348	5.193563	3.470401
H	2.740454	-0.343762	-1.728189
H	5.196234	-0.537089	-2.072652
H	5.789983	-0.187362	2.180795
H	3.333153	0.002504	2.492995
N	7.056508	-0.436061	-0.158118
H	7.590460	-0.754493	0.641826
H	7.359134	-0.889788	-1.011947

-NH_2 RE^{TS}

C	-3.450680	-0.984374	-0.087582
C	-2.338645	-0.148091	0.086758
C	-2.570440	1.225586	0.244620
C	-3.862485	1.751067	0.223581
C	-4.972065	0.907001	0.044355
C	-4.747439	-0.472072	-0.110582
C	-0.925855	-0.719763	0.112685
O	-0.808337	-1.969295	-0.031442
O	0.024344	0.112166	0.279175
Pd	2.393980	-1.543197	-0.640405
C	3.326294	-2.077805	1.109433
N	4.495116	-2.767694	1.275559
C	4.773568	-2.965146	2.618968
C	3.753872	-2.389614	3.311665
N	2.883359	-1.853768	2.378019
C	5.340416	-3.237548	0.184474
C	1.627489	-1.178019	2.724977
C	1.326930	-1.122882	-2.348001
N	0.543151	-1.916017	-3.126067
C	-0.149002	-1.166364	-4.064298
C	0.221912	0.129139	-3.881809
N	1.128357	0.134099	-2.834725
C	0.297669	-3.334575	-2.874461
C	1.661428	1.334130	-2.192672
H	1.500040	-2.744521	-0.439725
H	1.244306	1.400153	-1.182191
H	2.754930	1.288452	-2.158967
H	-0.078130	1.031384	-4.392565
H	-0.838428	-1.612382	-4.764594
H	5.656571	-3.485709	2.958354
H	3.573688	-2.317293	4.373795
H	1.367969	2.207953	-2.779416
H	-0.188648	-3.766690	-3.752911
H	1.247879	-3.842449	-2.699354
H	-0.343212	-3.432608	-1.992912
H	4.811591	-3.049068	-0.751949
H	6.296836	-2.703461	0.181366
H	5.525157	-4.311428	0.289762
H	1.836537	-0.385596	3.450479
H	1.177626	-0.749540	1.822880
H	0.931285	-1.901530	3.160004
H	-3.277200	-2.050309	-0.202217
H	-5.596699	-1.142314	-0.238872
H	-4.018851	2.820950	0.357441
H	-1.714085	1.877767	0.388934
N	-6.280960	1.421804	0.084826
H	-6.358668	2.399035	-0.172914
H	-6.970342	0.861541	-0.403391

-OMe

C	-2.957201	-0.000220	-1.199466
C	-2.555010	0.000060	0.147507
C	-3.543717	0.000223	1.136046
C	-4.903776	0.000110	0.807447
C	-5.286395	-0.000184	-0.540840
C	-4.304230	-0.000344	-1.544495
C	-1.093285	0.000170	0.535452
O	-0.788725	0.000390	1.752454
O	-0.262918	-0.000015	-0.443663
Pd	1.878541	0.000023	-0.045643
C	1.954003	2.045274	0.000935
N	2.234504	2.912494	-1.012692
C	2.150114	4.231192	-0.585503
C	1.816473	4.187577	0.731222
N	1.697855	2.847736	1.070108
C	2.527325	2.510469	-2.381618
C	1.376894	2.353699	2.410430
C	1.954127	-2.045235	0.001074
N	2.235361	-2.912358	-1.012468
C	2.150857	-4.231092	-0.585421
C	1.816368	-4.187621	0.731092
N	1.697419	-2.847807	1.070006
C	2.529192	-2.510254	-2.381149
C	1.375585	-2.353902	2.410170
H	3.427698	0.000162	0.146182
H	2.295438	2.077625	2.939007
H	0.866618	3.148512	2.961119
H	1.649753	4.979940	1.445193
H	2.323106	5.067011	-1.246562
H	2.324372	-5.066847	-1.246427
H	1.649233	-4.980041	1.444901
H	0.714741	1.487300	2.324070
H	1.668837	2.706692	-3.032894
H	3.400389	3.057738	-2.751261
H	2.739580	1.440500	-2.377843
H	2.740261	-1.440050	-2.377294
H	3.403262	-3.056591	-2.749799
H	1.671603	-2.707520	-3.033295
H	2.293894	-2.079512	2.940032
H	0.714880	-1.486456	2.323284
H	0.863284	-3.148104	2.959863
H	-3.233057	0.000444	2.176392
H	-5.643833	0.000258	1.600699
H	-4.622240	-0.000568	-2.583491
H	-2.192707	-0.000337	-1.969770
O	-6.585368	-0.000323	-0.977940
C	-7.624658	-0.000193	-0.011410
H	-8.558208	-0.000357	-0.577748
H	-7.582780	-0.896129	0.622639
H	-7.582886	0.895997	0.622288

-OMe HAA^{TS}

C	3.406525	-0.358970	-0.905209
C	2.879665	-0.157965	0.374585
C	3.770539	-0.060858	1.457473
C	5.143581	-0.160228	1.265939
C	5.659698	-0.362569	-0.024553
C	4.785885	-0.462486	-1.115965
C	1.390657	-0.048565	0.610055
O	0.969379	0.107897	1.779871
O	0.655502	-0.133295	-0.441816
Pd	-1.509130	0.126072	-0.087012
C	-1.301700	2.172504	-0.069341
N	-1.187415	2.973864	1.025088
C	-1.012200	4.299357	0.659762
C	-1.012523	4.334823	-0.699466
N	-1.189350	3.026053	-1.126066
C	-1.221335	2.481297	2.403779
C	-1.227099	2.616105	-2.524103
C	-1.885157	-1.897688	-0.025165
N	-1.659817	-2.747008	1.016146
C	-2.036253	-4.042414	0.695701
C	-2.503340	-4.010851	-0.580269
N	-2.402811	-2.694099	-1.003391
C	-1.144119	-2.343095	2.324767
C	-2.813723	-2.226131	-2.320862
O	-4.487737	0.518927	0.123413
O	-5.138967	-0.504181	-0.297877
H	-3.253866	0.322916	0.047784
H	-0.331142	2.971233	-3.042605
H	-2.119336	3.016703	-3.017348
H	-1.249424	1.526062	-2.554111
H	-0.896436	5.158765	-1.387301
H	-0.895366	5.088112	1.387424
H	-0.890998	3.284547	3.067123
H	-2.240642	2.187044	2.672010
H	-0.544600	1.626971	2.489024
H	-0.542721	-1.437241	2.212528
H	-1.974176	-2.161698	3.016560
H	-1.935053	-4.861164	1.392104
H	-0.513081	-3.144291	2.719842
H	-2.239798	-2.738146	-3.100277
H	-2.619303	-1.153875	-2.371216
H	-3.883103	-2.404340	-2.467834
H	-2.886608	-4.795832	-1.214691
H	3.361105	0.093400	2.450891
H	5.837582	-0.085623	2.098496
H	5.160825	-0.619371	-2.121684
H	2.722376	-0.437096	-1.744178
O	7.023530	-0.448731	-0.113861
C	7.607762	-0.660350	-1.390239
H	8.685706	-0.699682	-1.221397
H	7.272726	-1.608565	-1.831757
H	7.376223	0.163753	-2.078459

-OMe RE^{TS}

C	-3.489774	-1.006661	-0.160495
C	-2.396154	-0.164844	0.061596
C	-2.642690	1.208007	0.233667
C	-3.935735	1.719663	0.190120
C	-5.023037	0.860028	-0.032509
C	-4.799374	-0.511512	-0.209468
C	-0.972358	-0.713985	0.108221
O	-0.044099	0.119906	0.297280
O	-0.840908	-1.970815	-0.049148
Pd	2.027779	-2.389182	0.931064
C	3.078156	-2.709763	-0.804948
N	4.405157	-3.003472	-0.954312
C	4.746039	-3.113037	-2.293314
C	3.607766	-2.878570	-3.000568
N	2.603160	-2.635662	-2.079473
C	5.343279	-3.176860	0.148377
C	1.222123	-2.300172	-2.444996
C	0.960025	-1.896873	2.618421
N	-0.064322	-2.642120	3.119755
C	-0.714218	-1.975081	4.144900
C	-0.072885	-0.785766	4.298383
N	0.951678	-0.761112	3.365419
C	-0.520627	-3.889853	2.509858
C	1.768071	0.417317	3.082746
H	2.205352	-0.909712	0.680630
H	-0.861935	-3.673253	1.491971
H	0.292877	-4.622668	2.498556
H	-1.562748	-2.395111	4.663104
H	-0.257337	0.034744	4.974693
H	5.748741	-3.344945	-2.619932
H	3.428345	-2.861698	-4.065147
H	-1.343141	-4.293153	3.105442
H	1.724099	1.088940	3.944000
H	2.802110	0.111146	2.913939
H	1.376663	0.912557	2.189015
H	4.826659	-2.906396	1.071345
H	5.680606	-4.217408	0.206448
H	6.209405	-2.522040	0.009203
H	0.824015	-3.080741	-3.101068
H	0.608062	-2.225703	-1.540488
H	1.206906	-1.338604	-2.967271
H	-1.793692	1.864887	0.397078
H	-4.129841	2.781104	0.320430
H	-5.622619	-1.195811	-0.387298
H	-3.302012	-2.066904	-0.302160
O	-6.260170	1.456455	-0.061561
C	-7.395100	0.643674	-0.308546
H	-8.253840	1.318505	-0.300066
H	-7.330096	0.149310	-1.287615
H	-7.523443	-0.117751	0.473327

-Me

N	0.133973	0.383854	0.158446
C	-0.025301	-0.100795	1.421558
N	1.239174	-0.425203	1.818899
C	2.167699	-0.142395	0.825996
C	1.467857	0.363362	-0.222898
Pd	-1.774895	-0.261652	2.474541
C	-3.529346	-0.570919	3.476782
N	-3.764536	-0.508934	4.817173
C	-5.108542	-0.712735	5.101291
C	-5.727682	-0.911276	3.907381
N	-4.748363	-0.823505	2.929687
C	-2.748615	-0.208946	5.817511
C	-4.984897	-0.925411	1.488871
C	1.580866	-0.956140	3.131816
C	-0.955248	0.825793	-0.712140
O	-1.980352	1.896750	2.674378
C	-2.851039	2.505765	1.951336
O	-3.530014	1.987690	1.035394
C	-3.035188	3.979080	2.256269
C	-2.275753	4.623140	3.240927
C	-2.460704	5.983135	3.505545
C	-3.407174	6.737407	2.797609
C	-4.165635	6.084304	1.811445
C	-3.983116	4.728102	1.543259
C	-3.609299	8.209685	3.078730
H	-1.600237	-1.812148	2.417250
H	-4.419522	-1.768493	1.082353
H	-6.052832	-1.089311	1.323890
H	-6.764095	-1.098948	3.670963
H	-5.497860	-0.694259	6.108028
H	3.225289	-0.317321	0.954856
H	1.795611	0.707464	-1.192390
H	-4.663508	0.003468	1.009622
H	-2.944248	0.764792	6.278170
H	-2.738600	-0.985650	6.589502
H	-1.781791	-0.176863	5.313449
H	0.661205	-1.308146	3.601075
H	2.280620	-1.790768	3.022411
H	2.035390	-0.179120	3.756296
H	-1.149125	0.070743	-1.482165
H	-1.855398	0.987272	-0.114966
H	-0.674236	1.768666	-1.190780
H	-4.568948	4.225613	0.779592
H	-4.907769	6.647812	1.247483
H	-1.859736	6.466816	4.273963
H	-1.540406	4.045664	3.792324
H	-2.963423	8.553634	3.894056
H	-3.384074	8.820745	2.194620
H	-4.647990	8.425012	3.361711

-Me HAA^{TS}

N	-2.287540	-2.623497	-0.976833
C	-1.708503	-1.860491	-0.006672
N	-1.472981	-2.733386	1.012614
C	-1.902373	-4.010739	0.686610
C	-2.414060	-3.943487	-0.570816
Pd	-1.260926	0.148891	-0.052430
C	-0.978348	2.186596	-0.011638
N	-0.746821	2.959877	1.084491
C	-0.562435	4.287572	0.731460
C	-0.675048	4.352623	-0.621992
N	-0.928370	3.059428	-1.057391
C	-0.690975	2.441114	2.452575
C	-1.092593	2.681471	-2.455289
C	-0.896992	-2.365661	2.306711
C	-2.721783	-2.122919	-2.274778
O	0.867614	-0.187639	-0.526290
C	1.667959	-0.165746	0.479096
O	1.329046	-0.037552	1.678187
C	3.137792	-0.313285	0.143002
C	3.574068	-0.476516	-1.177689
C	4.935373	-0.608733	-1.464685
C	5.897440	-0.581315	-0.445123
C	5.451675	-0.417388	0.877251
C	4.094508	-0.286026	1.168675
C	7.371689	-0.724012	-0.751043
O	-4.208060	0.656938	0.304546
O	-4.920953	-0.287397	-0.193477
H	-2.988562	0.411948	0.169338
H	-0.216723	2.991929	-3.033493
H	-1.992307	3.145193	-2.873755
H	-1.184962	1.595572	-2.501180
H	-0.590221	5.187415	-1.301283
H	-0.360980	5.056554	1.461808
H	-0.212120	3.189800	3.088749
H	-1.702078	2.244600	2.823139
H	-0.097822	1.522916	2.455098
H	-0.243914	-1.498572	2.177956
H	-1.694204	-2.135156	3.022078
H	-1.803147	-4.843423	1.366560
H	-0.306382	-3.205918	2.682445
H	-2.151045	-2.602425	-3.076984
H	-2.544528	-1.046840	-2.295388
H	-3.790152	-2.313235	-2.412629
H	-2.844797	-4.705474	-1.202805
H	3.752681	-0.160219	2.191402
H	6.179103	-0.393107	1.687445
H	5.255609	-0.736102	-2.497366
H	2.835679	-0.499902	-1.972867
H	7.547007	-0.849640	-1.825027
H	7.936450	0.157857	-0.421206
H	7.804473	-1.592835	-0.238067

-Me RE^{TS}

N	-3.493730	-0.997271	-0.064181
C	-2.420911	-0.181939	0.117424
N	-2.958081	1.063060	0.249829
C	-4.340366	1.023387	0.174371
C	-4.678465	-0.278987	-0.022221
Pd	-0.433365	-0.618985	0.415673
C	1.494925	-1.200097	0.817263
N	2.449791	-1.645994	-0.053774
C	3.618804	-1.979051	0.612332
C	3.390632	-1.740770	1.932164
N	2.094382	-1.266388	2.038646
C	2.266179	-1.759315	-1.495805
C	1.449937	-0.929734	3.313678
C	-2.172278	2.239759	0.616740
C	-3.426706	-2.457024	-0.090593
O	-1.480563	0.349535	3.117017
C	-2.228721	-0.627293	3.440488
O	-2.190272	-1.793949	2.960760
C	-3.279501	-0.355708	4.518570
C	-3.395678	0.906829	5.112577
C	-4.358156	1.149788	6.097643
C	-5.232086	0.138599	6.521445
C	-5.111033	-1.127041	5.923599
C	-4.150865	-1.370877	4.940737
C	-6.263010	0.390541	7.599791
H	-0.858478	-1.994926	0.872522
H	-1.734814	2.069725	1.606128
H	-1.389610	2.416257	-0.128335
H	-4.951439	1.907774	0.271090
H	-5.643369	-0.750586	-0.127932
H	4.494600	-2.347135	0.099154
H	4.029128	-1.867466	2.793596
H	-2.831727	3.110611	0.640943
H	-4.379470	-2.844388	-0.460716
H	-2.623093	-2.771884	-0.758755
H	-3.231267	-2.822386	0.922175
H	1.218132	-1.547653	-1.716649
H	2.905545	-1.042545	-2.022458
H	2.510759	-2.774050	-1.825716
H	2.085686	-0.226648	3.860885
H	0.470310	-0.478059	3.124721
H	1.313001	-1.840028	3.905284
H	-4.055231	-2.351703	4.484443
H	-5.776765	-1.931079	6.236230
H	-4.429684	2.139449	6.547174
H	-2.716444	1.691424	4.792415
H	-6.313964	1.452913	7.863526
H	-7.265128	0.075749	7.281026
H	-6.027995	-0.166955	8.516832

-H

N	-0.081487	0.193690	-0.092417
C	-0.082805	0.045267	1.262689
N	1.234000	-0.057315	1.592879
C	2.040389	0.026934	0.466824
C	1.211332	0.179601	-0.599107
Pd	-1.687859	-0.046148	2.528390
O	-1.684585	-2.227767	2.569853
C	-1.049431	-2.789168	3.540219
C	-1.126031	-4.305261	3.576748
C	1.736927	-0.183733	2.961865
C	-1.284169	0.303324	-0.907559
C	-3.262698	-0.004671	3.830902
N	-4.462620	-0.636317	3.702226
C	-5.254549	-0.445201	4.825467
C	-4.529789	0.317661	5.685889
N	-3.320689	0.582396	5.058185
C	-4.861779	-1.400106	2.522723
C	-2.205986	1.289455	5.679729
O	-0.394732	-2.194745	4.421059
H	-1.768751	1.510455	2.424960
H	-1.611949	1.754970	4.892083
H	-2.597581	2.056363	6.354229
H	-4.759702	0.681611	6.675829
H	-6.244899	-0.865751	4.913626
H	1.421326	0.268901	-1.654357
H	3.116805	-0.034446	0.522613
H	-1.575407	0.589161	6.236536
H	-5.598089	-2.151549	2.820486
H	-5.302588	-0.739676	1.768056
H	-3.978728	-1.897790	2.119039
H	-2.125105	0.494000	-0.238865
H	-1.180187	1.132923	-1.614285
H	-1.461296	-0.626394	-1.459122
H	1.913696	0.808773	3.390939
H	1.007952	-0.731195	3.566058
H	2.677677	-0.740858	2.940044
C	-0.529795	-5.002372	4.637360
C	-0.586178	-6.397138	4.690557
C	-1.237048	-7.112322	3.678991
C	-1.831329	-6.424011	2.615629
C	-1.777100	-5.028417	2.566663
H	-0.025675	-4.429920	5.409898
H	-0.121756	-6.927341	5.519089
H	-1.279406	-8.198520	3.718151
H	-2.335322	-6.975425	1.824771
H	-2.231268	-4.482345	1.745992

-H HAA^{TS}

N	-2.899382	0.003046	1.018237
C	-2.068125	-0.447285	0.037391
N	-2.897929	-1.061777	-0.852321
C	-4.220214	-0.988787	-0.440658
C	-4.219752	-0.314966	0.739867
Pd	-0.022033	-0.234638	-0.047338
O	0.350396	-1.978385	1.251397
C	0.489663	-1.735845	2.504929
O	0.390697	-0.612216	3.048946
C	-2.461787	-1.685557	-2.095156
C	-2.464346	0.764976	2.189764
C	1.992145	0.163741	-0.203177
N	2.728609	0.987682	0.592310
C	4.062874	0.986465	0.216468
C	4.172632	0.135875	-0.838400
N	2.897558	-0.355826	-1.080264
C	2.172483	1.779335	1.691699
C	2.577152	-1.328497	-2.116885
C	0.799848	-2.944525	3.368317
O	-0.507692	1.931312	-2.083160
O	-1.606286	1.746838	-2.720487
H	-0.338514	1.039137	-1.221132
H	3.117423	-2.263845	-1.939002
H	2.841031	-0.932706	-3.103121
H	1.504184	-1.520455	-2.075753
H	5.030158	-0.162863	-1.422313
H	4.807374	1.576488	0.729275
H	2.989408	2.074726	2.355093
H	1.682006	2.676432	1.300068
H	1.457651	1.163625	2.244052
H	-1.457251	0.447196	2.472261
H	-2.474520	1.837522	1.967015
H	-5.029407	-0.046202	1.401451
H	-3.150411	0.561157	3.016461
H	-2.866280	-2.700105	-2.165526
H	-1.371953	-1.730005	-2.084458
H	-2.790152	-1.092048	-2.953924
H	-5.029038	-1.422141	-1.009419
C	0.968244	-2.783401	4.750931
C	1.258559	-3.883271	5.561722
C	1.383469	-5.157517	4.997164
C	1.215326	-5.325284	3.618219
C	0.924836	-4.224378	2.808474
H	0.867860	-1.787259	5.170531
H	1.387598	-3.747721	6.633206
H	1.609772	-6.014324	5.627757
H	1.310382	-6.314084	3.174988
H	0.790910	-4.339410	1.737704

-H RE^{TS}

N	-3.328401	-0.885072	-0.330459
C	-2.271286	-0.068941	-0.061912
N	-2.805523	1.180912	-0.033657
C	-4.164721	1.148412	-0.302170
C	-4.496147	-0.157312	-0.487615
Pd	-0.310794	-0.690588	0.001560
C	1.686083	-1.167395	-0.044007
N	2.568221	-1.240443	0.998077
C	3.840667	-1.565241	0.554593
C	3.755318	-1.694027	-0.797089
N	2.437621	-1.449747	-1.143950
C	2.220692	-1.006137	2.394519
C	1.942118	-1.450375	-2.525925
C	-2.022097	2.411136	0.058468
C	-3.190208	-2.316465	-0.594869
O	-1.213526	-1.206094	-2.892874
C	-1.391502	-0.007980	-3.280449
O	-0.853496	1.026470	-2.799296
C	-2.366536	0.194715	-4.444801
H	0.089228	0.676960	-0.502474
H	-2.552076	-2.446367	-1.475292
H	-2.758309	-2.820505	0.275914
H	-5.441752	-0.622441	-0.720728
H	-4.766149	2.043389	-0.345188
H	4.678516	-1.677417	1.226367
H	4.508205	-1.934502	-1.532712
H	-4.180760	-2.736813	-0.783949
H	-2.696882	3.240129	0.286928
H	-1.284708	2.312540	0.857049
H	-1.514104	2.582258	-0.895488
H	1.187323	-0.655335	2.427476
H	2.314580	-1.930530	2.974635
H	2.878197	-0.241948	2.821175
H	2.235643	-2.387306	-3.009466
H	0.850441	-1.356706	-2.528013
H	2.373926	-0.604142	-3.068955
C	-2.626310	1.481126	-4.938969
C	-3.518744	1.672448	-5.997632
C	-4.164164	0.574958	-6.579038
C	-3.907345	-0.713161	-6.096024
C	-3.013510	-0.899337	-5.037183
H	-2.111535	2.319562	-4.479371
H	-3.709489	2.676139	-6.372616
H	-4.857767	0.721893	-7.404290
H	-4.400917	-1.571455	-6.547938
H	-2.796235	-1.892227	-4.654776

-F

C	-3.790635	4.810780	1.397919
C	-2.968771	4.029046	2.222393
C	-2.323529	4.633776	3.311045
C	-2.492090	5.994408	3.579063
C	-3.316600	6.734392	2.739003
C	-3.972745	6.172453	1.649628
C	-2.795148	2.551363	1.928139
O	-3.387080	2.062189	0.938391
O	-2.033768	1.914565	2.740804
Pd	-1.806482	-0.239915	2.499811
C	-3.557018	-0.599218	3.496286
N	-3.775672	-0.684156	4.838382
C	-5.119065	-0.900285	5.116716
C	-5.755878	-0.954466	3.917038
N	-4.787796	-0.767368	2.941614
C	-2.741337	-0.530924	5.852658
C	-5.042348	-0.742629	1.500124
C	-0.073135	-0.045409	1.427011
N	0.043305	0.277844	0.109352
C	1.374684	0.337425	-0.276532
C	2.115769	0.051200	0.825808
N	1.213792	-0.185436	1.854868
C	-1.087120	0.475833	-0.798916
C	1.595340	-0.492452	3.226877
H	-1.608753	-1.785100	2.414655
H	-4.646440	-1.650965	1.035787
H	-6.122453	-0.693592	1.339954
H	-6.798195	-1.098155	3.675713
H	-5.496208	-0.985116	6.124713
H	3.184710	0.003770	0.969547
H	1.672095	0.578730	-1.285903
H	-4.562156	0.140035	1.068754
H	-2.946616	0.345812	6.475505
H	-2.693179	-1.425212	6.483123
H	-1.789036	-0.391980	5.339312
H	0.718436	-0.893271	3.737383
H	2.395523	-1.239176	3.229425
H	1.936888	0.410408	3.744763
H	-1.359932	-0.473287	-1.273284
H	-1.937143	0.873136	-0.237849
H	-0.797496	1.195801	-1.569426
H	-4.283996	4.331934	0.558159
H	-4.606461	6.791799	1.022016
H	-1.999956	6.479143	4.416919
H	-1.688490	4.022390	3.943580
F	-3.488232	8.063505	2.993672

-F HAA^{TS}

C	3.424943	-0.230953	-0.926686
C	2.887613	-0.125709	0.364337
C	3.754292	-0.135606	1.467143
C	5.135213	-0.250374	1.291610
C	5.628789	-0.354353	-0.004100
C	4.802737	-0.346784	-1.122527
C	1.386923	-0.008656	0.545072
O	0.655238	-0.004115	-0.471120
O	0.986040	0.077820	1.761552
Pd	-1.204168	0.154893	2.048625
C	-1.338839	-1.899206	1.992475
N	-1.587550	-2.674491	0.901225
C	-1.569936	-4.021440	1.228633
C	-1.297072	-4.098294	2.558301
N	-1.159874	-2.792153	3.006901
C	-1.847244	-2.144364	-0.438854
C	-0.835946	-2.427097	4.380046
C	-1.274071	2.213011	2.076087
N	-1.297925	3.049292	3.152182
C	-1.358208	4.377092	2.756665
C	-1.367444	4.374418	1.397474
N	-1.310795	3.047445	0.999834
C	-1.299327	2.609237	4.541591
C	-1.337956	2.603832	-0.394601
O	-4.132004	0.227001	2.742813
O	-4.451144	1.312140	3.348748
H	-2.919157	0.228959	2.437510
H	0.128102	-2.857978	4.668509
H	-1.616019	-2.781690	5.061807
H	-0.772462	-1.339385	4.431904
H	-1.183138	-4.950844	3.210773
H	-1.742791	-4.795759	0.496571
H	-1.690565	-2.945281	-1.165905
H	-2.879910	-1.787896	-0.510276
H	-1.147553	-1.328347	-0.637245
H	-0.796924	1.658019	-0.481655
H	-2.373227	2.480601	-0.730980
H	-1.399439	5.187978	0.688550
H	-0.844305	3.357870	-1.013886
H	-0.526671	3.143717	5.102956
H	-1.083451	1.540099	4.555954
H	-2.279427	2.785630	4.995496
H	-1.380310	5.192164	3.464229
H	2.744692	-0.221494	-1.772229
H	5.235687	-0.430032	-2.114786
H	5.821210	-0.259802	2.133221
H	3.331887	-0.052042	2.462950
F	6.975278	-0.468047	-0.184802

-F RE^{TS}

N	1.089440	0.128856	-2.800321
C	1.305983	-1.129044	-2.324265
N	0.517674	-1.924666	-3.094939
C	-0.194875	-1.175786	-4.018300
C	0.167513	0.121861	-3.833764
Pd	2.405209	-1.552109	-0.638569
C	3.356529	-2.080782	1.102782
N	4.533327	-2.758260	1.260273
C	4.822823	-2.953242	2.601673
C	3.801759	-2.389029	3.301581
N	2.919226	-1.862191	2.374087
C	5.377053	-3.218152	0.163426
C	1.658393	-1.200638	2.730386
C	0.291265	-3.347979	-2.851842
C	1.624777	1.330643	-2.163166
O	-0.017644	0.106520	0.317907
C	-0.956213	-0.733547	0.146950
O	-0.838247	-1.981996	0.013172
C	-2.377202	-0.165368	0.097176
C	-3.476891	-1.015774	-0.087325
C	-4.779646	-0.511795	-0.137109
C	-4.960586	0.859377	0.003303
C	-3.899752	1.737294	0.193061
C	-2.605483	1.210685	0.239676
F	-6.230318	1.363484	-0.044686
H	1.511394	-2.750447	-0.420723
H	1.217784	1.396554	-1.148795
H	2.718587	1.288458	-2.140125
H	-0.147456	1.024166	-4.335334
H	-0.890040	-1.623760	-4.711632
H	5.713681	-3.464320	2.934849
H	3.628117	-2.319095	4.364944
H	1.323267	2.203455	-2.747170
H	-0.194918	-3.780099	-3.730236
H	1.248626	-3.845219	-2.686132
H	-0.343372	-3.461523	-1.967742
H	4.840676	-3.036884	-0.770006
H	6.326858	-2.672648	0.154062
H	5.575269	-4.289617	0.267704
H	1.863992	-0.403739	3.451852
H	1.194938	-0.779573	1.832216
H	0.975009	-1.931363	3.173556
H	-3.290546	-2.080580	-0.186847
H	-5.640807	-1.158661	-0.277835
H	-4.092007	2.800624	0.303790
H	-1.749479	1.860458	0.392852

-Cl

N	0.042331	0.283904	0.111644
C	-0.074186	-0.042751	1.428433
N	1.212684	-0.185987	1.855495
C	2.114645	0.051869	0.826753
C	1.373711	0.342264	-0.274573
Pd	-1.807209	-0.239639	2.501384
C	-3.558063	-0.602464	3.496282
N	-3.778766	-0.684655	4.838164
C	-5.121935	-0.904440	5.114667
C	-5.756404	-0.963924	3.914026
N	-4.787205	-0.776676	2.939807
C	-2.746809	-0.524860	5.853948
C	-5.039506	-0.754072	1.497775
C	1.594368	-0.497209	3.226575
C	-1.087868	0.485253	-0.796132
O	-2.040188	1.915517	2.746826
C	-2.801921	2.551322	1.934538
O	-3.396906	2.063086	0.946669
C	-2.971020	4.030845	2.226560
C	-2.315108	4.638802	3.305807
C	-2.477143	6.000638	3.568930
C	-3.307193	6.755597	2.738471
C	-3.971882	6.175497	1.656707
C	-3.797086	4.812764	1.408164
H	-1.608964	-1.784013	2.411890
H	-4.627885	-1.655245	1.033339
H	-6.119941	-0.722584	1.335731
H	-6.797804	-1.111715	3.671253
H	-5.500602	-0.987928	6.122196
H	3.183559	0.002020	0.969927
H	1.671253	0.585649	-1.283401
H	-4.572134	0.136265	1.068176
H	-2.960586	0.348703	6.478332
H	-2.691454	-1.419908	6.482767
H	-1.795164	-0.376458	5.342045
H	0.716904	-0.897062	3.736870
H	2.392670	-1.245916	3.226743
H	1.938478	0.403657	3.746190
H	-1.358661	-0.461653	-1.276034
H	-1.939130	0.877882	-0.233713
H	-0.799116	1.210025	-1.562453
H	-4.300602	4.334661	0.573812
H	-4.612871	6.780256	1.022657
H	-1.968414	6.471843	4.404290
H	-1.675069	4.030158	3.936222
Cl	-3.519376	8.476128	3.062375

-Cl HAA^{TS}

N	3.407849	-0.342083	-0.907174
C	2.893092	-0.161523	0.342135
N	3.985482	-0.133535	1.155853
C	5.154609	-0.301613	0.429592
C	4.791311	-0.431160	-0.873654
Pd	0.919929	0.034556	0.899895
C	-1.050564	0.038497	1.495154
N	-1.525857	-0.178550	2.752170
C	-2.905894	-0.055482	2.794447
C	-3.310861	0.251332	1.533305
N	-2.163300	0.304967	0.754629
C	-0.676338	-0.486509	3.904386
C	-2.150555	0.629055	-0.666394
C	3.936040	-0.003438	2.612561
C	2.611993	-0.450031	-2.123329
O	1.023211	2.239865	1.058625
C	1.217379	2.693510	2.243373
O	1.404762	2.005401	3.271957
C	1.216783	4.205539	2.366511
C	1.043117	5.027707	1.244639
C	1.044130	6.418494	1.368723
C	1.219887	6.984856	2.632504
C	1.394986	6.188691	3.765776
C	1.392976	4.799970	3.623201
O	0.676799	-2.929683	0.443445
O	1.568480	-3.364668	-0.370492
H	0.812199	-1.702718	0.635883
H	-2.639571	1.593373	-0.835716
H	-2.664592	-0.148905	-1.240934
H	-1.110112	0.694205	-0.987102
H	-4.294545	0.440746	1.130852
H	-3.469643	-0.186298	3.705689
H	-1.267526	-0.361469	4.814984
H	-0.319828	-1.519452	3.843642
H	0.168049	0.207398	3.914498
H	3.029794	0.537462	2.896309
H	3.945565	-0.994372	3.079753
H	6.127842	-0.308108	0.896830
H	4.809933	0.562236	2.947768
H	2.906549	0.325865	-2.837400
H	1.564117	-0.315004	-1.851763
H	2.742000	-1.438937	-2.573032
H	5.384844	-0.570501	-1.764634
H	1.528476	4.156318	4.486567
H	1.530452	6.648751	4.739677
H	0.911278	7.055801	0.499995
H	0.908960	4.564274	0.272714
Cl	1.221460	8.739411	2.800083

-Cl RE^{TS}

N	-3.490514	-1.004747	-0.101938
C	-2.420885	-0.189102	0.095093
N	-2.960465	1.054892	0.226319
C	-4.341723	1.014302	0.133985
C	-4.676246	-0.287682	-0.071629
Pd	-0.435754	-0.625565	0.407020
C	1.490491	-1.201716	0.825834
N	2.448920	-1.658606	-0.035146
C	3.616312	-1.978692	0.640010
C	3.383264	-1.720883	1.955305
N	2.085466	-1.248273	2.050175
C	2.271016	-1.793806	-1.476200
C	1.436631	-0.891205	3.317256
C	-2.179881	2.232737	0.601289
C	-3.421456	-2.464243	-0.133964
O	-1.508665	0.354279	3.136840
C	-2.273006	-0.611783	3.449672
O	-2.265844	-1.773384	2.960591
C	-3.313940	-0.328685	4.537610
C	-3.396790	0.932466	5.142754
C	-4.345924	1.198250	6.133336
C	-5.219617	0.181021	6.520035
C	-5.157626	-1.087147	5.940275
C	-4.201281	-1.331358	4.951598
H	-0.864656	-1.998602	0.868872
H	-1.747830	2.062362	1.592835
H	-1.393232	2.413865	-0.138370
H	-4.954774	1.898006	0.224506
H	-5.639390	-0.759450	-0.191810
H	4.494424	-2.353155	0.135506
H	4.019216	-1.833021	2.820625
H	-2.841751	3.101707	0.623998
H	-4.368361	-2.851324	-0.518831
H	-2.608412	-2.775406	-0.792274
H	-3.240058	-2.834223	0.879625
H	1.221666	-1.596594	-1.703737
H	2.904336	-1.077622	-2.010765
H	2.527679	-2.810297	-1.790851
H	2.056576	-0.159028	3.844071
H	0.446908	-0.466333	3.119226
H	1.322705	-1.787938	3.933975
H	-4.125229	-2.309246	4.486021
H	-5.843293	-1.866443	6.259651
H	-4.407141	2.176369	6.601365
H	-2.699569	1.702449	4.826882
Cl	-6.425786	0.503961	7.769902

-CF_3

C	-3.805740	4.811027	1.393970
C	-2.987536	4.026834	2.215597
C	-2.321900	4.630763	3.292989
C	-2.471464	5.992705	3.544122
C	-3.293462	6.768654	2.714787
C	-3.962122	6.177010	1.638350
C	-2.828826	2.541746	1.927803
O	-3.427326	2.056972	0.941590
O	-2.069607	1.908198	2.742079
Pd	-1.811491	-0.248130	2.506962
C	-3.559550	-0.629880	3.501108
N	-3.780498	-0.723318	4.842205
C	-5.122220	-0.955081	5.116045
C	-5.755407	-1.010679	3.914647
N	-4.787074	-0.809007	2.942481
C	-2.750642	-0.565852	5.860609
C	-5.039426	-0.780454	1.500524
C	-0.079635	-0.036855	1.434117
N	0.034601	0.287029	0.116494
C	1.365601	0.355175	-0.269542
C	2.108414	0.074747	0.833070
N	1.208157	-0.167052	1.862351
C	-1.096637	0.474742	-0.792874
C	1.592597	-0.470377	3.234545
H	-1.595141	-1.789390	2.424005
H	-4.619502	-1.674996	1.030698
H	-6.120123	-0.758839	1.338747
H	-6.795434	-1.164865	3.670003
H	-5.500876	-1.048871	6.122663
H	3.177646	0.034558	0.976867
H	1.661546	0.597792	-1.279011
H	-4.581754	0.116900	1.075098
H	-2.969321	0.302248	6.490857
H	-2.692510	-1.465016	6.483181
H	-1.798809	-0.410252	5.351338
H	0.717645	-0.872164	3.747525
H	2.394407	-1.215259	3.237317
H	1.932838	0.434528	3.749609
H	-1.361037	-0.476965	-1.266696
H	-1.950749	0.865045	-0.233640
H	-0.812685	1.196484	-1.563776
H	-4.313891	4.332847	0.562830
H	-4.598044	6.777616	0.996158
H	-1.952555	6.455478	4.379234
H	-1.688363	4.015918	3.923356
C	-3.434219	8.236233	3.008427
F	-4.250090	8.877461	2.137264
F	-3.937962	8.462958	4.254868
F	-2.234659	8.882752	2.969161

-CF_3 HAA^{TS}

N	-2.089134	-2.764343	1.008618
C	-2.326417	-1.916743	-0.031330
N	-2.830666	-2.718705	-1.011579
C	-2.912079	-4.037514	-0.590868
C	-2.445849	-4.064750	0.685433
Pd	-1.985853	0.114629	-0.086334
C	-1.822274	2.166661	-0.057725
N	-1.718354	2.962729	1.041595
C	-1.577693	4.294631	0.684375
C	-1.589448	4.339326	-0.674444
N	-1.738605	3.029765	-1.109090
C	-1.735573	2.461490	2.417414
C	-1.778477	2.630181	-2.510401
C	-3.250939	-2.254555	-2.327767
C	-1.582269	-2.355241	2.318915
O	0.191648	-0.102574	-0.446481
C	0.930994	-0.012988	0.596970
O	0.533547	0.131634	1.774026
C	2.426941	-0.101053	0.339181
C	3.322133	0.013330	1.411195
C	4.698016	-0.067162	1.198988
C	5.190518	-0.269318	-0.096189
C	4.305016	-0.383384	-1.174642
C	2.930241	-0.300133	-0.953588
O	-4.965438	0.444725	0.152447
O	-5.598383	-0.601688	-0.235463
H	-3.732174	0.275035	0.064379
H	-0.888622	2.998048	-3.030430
H	-2.676818	3.026064	-2.995954
H	-1.790918	1.540299	-2.549340
H	-1.498493	5.170514	-1.357316
H	-1.474829	5.081089	1.416607
H	-1.414317	3.265797	3.083785
H	-2.747980	2.148736	2.690603
H	-1.044414	1.618386	2.494943
H	-0.996835	-1.439138	2.209982
H	-2.415837	-2.189478	3.010232
H	-2.332997	-4.883351	1.380196
H	-0.937933	-3.146106	2.713155
H	-2.681146	-2.767741	-3.109217
H	-3.058792	-1.182126	-2.382847
H	-4.320844	-2.435411	-2.467578
H	-3.282899	-4.826914	-1.227170
H	2.919745	0.162527	2.407822
H	5.385765	0.018545	2.034745
H	4.688588	-0.543555	-2.177609
H	2.230774	-0.392370	-1.777602
C	6.674820	-0.305563	-0.335912
F	7.360570	-0.811907	0.721041
F	7.009666	-1.053702	-1.418587
F	7.187608	0.939168	-0.560309

-CF_3 RE^{TS}

C	-3.522611	-0.975511	-0.166582
C	-2.412554	-0.162590	0.101771
C	-2.619536	1.199092	0.359662
C	-3.904286	1.743880	0.344795
C	-5.004075	0.921068	0.071990
C	-4.811523	-0.442697	-0.185632
C	-0.996867	-0.757136	0.113550
O	-0.902274	-1.992313	-0.111223
O	-0.051235	0.058091	0.346158
Pd	2.425890	-1.573214	-0.645284
C	3.384512	-2.072585	1.101460
N	4.558030	-2.754519	1.262987
C	4.860658	-2.917799	2.605639
C	3.851410	-2.328812	3.302243
N	2.962104	-1.819689	2.371311
C	5.386540	-3.248620	0.169164
C	1.713104	-1.134744	2.724112
C	1.324276	-1.175040	-2.334850
N	0.566928	-1.991123	-3.114428
C	-0.159891	-1.260792	-4.041078
C	0.162296	0.046519	-3.849722
N	1.075103	0.077639	-2.808575
C	0.376154	-3.419612	-2.873122
C	1.572664	1.293703	-2.167101
H	1.535990	-2.772763	-0.415977
H	1.160781	1.346920	-1.154003
H	2.667117	1.284530	-2.140482
H	-0.173922	0.940430	-4.352574
H	-0.836036	-1.726919	-4.741223
H	5.750832	-3.427960	2.942037
H	3.690061	-2.230922	4.365327
H	1.247114	2.158187	-2.750443
H	-0.077278	-3.867926	-3.760785
H	1.343432	-3.888430	-2.684286
H	-0.275279	-3.548668	-2.003668
H	4.838193	-3.095226	-0.762200
H	6.336545	-2.704891	0.130492
H	5.585013	-4.316573	0.303643
H	1.939693	-0.283460	3.373744
H	1.213048	-0.783346	1.815139
H	1.052556	-1.831078	3.249813
H	-3.352173	-2.030957	-0.354020
H	-5.665365	-1.082111	-0.390769
H	-4.054050	2.799434	0.551495
H	-1.755047	1.818322	0.577252
C	-6.384583	1.507355	-0.002981
F	-6.522522	2.627073	0.754122
F	-6.723196	1.869777	-1.277150
F	-7.346175	0.637203	0.404637

-NO_2

N	0.011651	0.281418	0.115896
C	-0.096632	-0.007303	1.442028
N	1.192991	-0.091626	1.875534
C	2.088729	0.144045	0.840872
C	1.341103	0.373550	-0.270255
Pd	-1.826381	-0.237117	2.516001
C	-3.567747	-0.649986	3.512191
N	-3.769475	-0.823695	4.848473
C	-5.108464	-1.063693	5.128245
C	-5.759734	-1.043946	3.935574
N	-4.804957	-0.787726	2.962594
C	-2.725142	-0.729412	5.859964
C	-5.079074	-0.691300	1.527560
C	1.583691	-0.347576	3.255652
C	-1.124214	0.416386	-0.797305
O	-2.103415	1.918399	2.754387
C	-2.828524	2.566810	1.923144
O	-3.409164	2.103069	0.917101
C	-2.972746	4.053601	2.218790
C	-2.334511	4.634635	3.325158
C	-2.468900	5.995763	3.590694
C	-3.252392	6.770981	2.732198
C	-3.899125	6.220243	1.623026
C	-3.752563	4.857184	1.373935
N	-3.399917	8.208586	3.004292
H	-1.593013	-1.774351	2.428940
H	-4.754754	-1.606085	1.021566
H	-6.155304	-0.561227	1.388022
H	-6.803973	-1.179391	3.697778
H	-5.472757	-1.214940	6.133178
H	3.158335	0.135828	0.987149
H	1.632701	0.595496	-1.285704
H	-4.548629	0.173148	1.119515
H	-2.899482	0.134979	6.509125
H	-2.702003	-1.642235	6.464279
H	-1.771494	-0.606622	5.345057
H	0.709971	-0.727539	3.786828
H	2.382746	-1.095010	3.281843
H	1.929260	0.574041	3.736201
H	-1.398695	-0.562474	-1.204982
H	-1.971045	0.849690	-0.259365
H	-0.839076	1.082610	-1.616050
H	-4.238417	4.392313	0.522463
H	-4.498209	6.853935	0.979746
H	-1.982339	6.459677	4.440593
H	-1.733495	4.002223	3.969427
O	-2.822746	8.673563	3.991241
O	-4.093088	8.876295	2.232044

-NO_2 HAA^{TS}

N	-2.571250	-2.710240	-0.991827
C	-2.053554	-1.908919	-0.018301
N	-1.818305	-2.753889	1.024196
C	-2.189740	-4.052229	0.709240
C	-2.663247	-4.026197	-0.564393
Pd	-1.695715	0.119634	-0.083010
C	-1.519130	2.171338	-0.060813
N	-1.396944	2.969047	1.035472
C	-1.256628	4.299829	0.673726
C	-1.287047	4.341911	-0.684865
N	-1.446955	3.032087	-1.114877
C	-1.400238	2.471413	2.412707
C	-1.509410	2.630624	-2.514960
C	-1.300083	-2.343364	2.329558
C	-2.996349	-2.247940	-2.307252
O	0.479638	-0.116296	-0.466884
C	1.231122	-0.032532	0.566773
O	0.854934	0.114748	1.749768
C	2.724482	-0.131376	0.288300
C	3.206005	-0.338834	-1.013192
C	4.574640	-0.429804	-1.258559
C	5.456985	-0.308552	-0.182475
C	5.006288	-0.101724	1.123464
C	3.634240	-0.015502	1.349699
N	6.903852	-0.401633	-0.432328
O	-4.667965	0.471638	0.191089
O	-5.312271	-0.571509	-0.185542
H	-3.438447	0.293474	0.089016
H	-0.625053	2.992336	-3.048474
H	-2.412215	3.031347	-2.987975
H	-1.529357	1.540793	-2.552291
H	-1.202940	5.171510	-1.370543
H	-1.141222	5.087392	1.402896
H	-1.062850	3.274287	3.072743
H	-2.411572	2.168378	2.700385
H	-0.715791	1.622467	2.484038
H	-0.703585	-1.435626	2.212081
H	-2.127960	-2.162392	3.023813
H	-2.080860	-4.868734	1.407089
H	-0.664189	-3.139968	2.725843
H	-2.443189	-2.776537	-3.090284
H	-2.786203	-1.179454	-2.372154
H	-4.070519	-2.411256	-2.435489
H	-3.045574	-4.814830	-1.194796
H	3.244687	0.142121	2.349867
H	5.721974	-0.013004	1.932281
H	4.963275	-0.591272	-2.257105
H	2.492499	-0.428801	-1.825007
O	7.279937	-0.583843	-1.593348
O	7.665626	-0.292473	0.531934

-NO_2 RE^{TS}

N	-3.468796	-1.017485	-0.185038
C	-2.408041	-0.199754	0.045512
N	-2.957097	1.037346	0.199323
C	-4.336857	0.989400	0.089242
C	-4.659538	-0.309633	-0.151601
Pd	-0.423999	-0.630391	0.367449
C	1.500990	-1.192679	0.811345
N	2.467245	-1.662330	-0.033219
C	3.631887	-1.960418	0.656441
C	3.388958	-1.675289	1.964252
N	2.087431	-1.209418	2.040413
C	2.299453	-1.832446	-1.472119
C	1.430780	-0.822039	3.294214
C	-2.190552	2.213120	0.608970
C	-3.390157	-2.475313	-0.246979
O	-1.563343	0.312149	3.164299
C	-2.362271	-0.633645	3.441939
O	-2.431125	-1.766477	2.898927
C	-3.364088	-0.356475	4.574626
C	-3.365814	0.878361	5.241323
C	-4.274259	1.139244	6.265288
C	-5.187838	0.142382	6.619713
C	-5.207611	-1.099826	5.978557
C	-4.290120	-1.338877	4.957595
N	-6.152033	0.407199	7.694357
H	-0.854403	-2.000809	0.836390
H	-1.777712	2.031175	1.606482
H	-1.389909	2.410008	-0.111210
H	-4.957067	1.866983	0.190224
H	-5.617627	-0.784851	-0.296175
H	4.515220	-2.341474	0.166191
H	4.020133	-1.764256	2.835722
H	-2.857191	3.078373	0.630899
H	-4.321064	-2.859342	-0.671652
H	-2.553836	-2.767117	-0.884438
H	-3.240981	-2.866088	0.763918
H	1.251884	-1.641930	-1.712526
H	2.936147	-1.128766	-2.018861
H	2.558951	-2.855948	-1.760257
H	2.012778	-0.031299	3.778027
H	0.418172	-0.460416	3.086955
H	1.372151	-1.690784	3.957030
H	-4.270793	-2.291413	4.438106
H	-5.927740	-1.850221	6.283458
H	-4.285854	2.088809	6.787669
H	-2.638222	1.625161	4.940634
O	-6.115750	1.509693	8.250236
O	-6.953708	-0.484689	7.989655

X-ray crystallographic Analysis of $(IMes)_2Pd(H)(O_2CC_6H_4$-*p*$Me)$, 1d.

Data Collection

A colorless crystal with approximate dimensions 0.40 x 0.35 x 0.12 mm^3 was selected under oil under ambient conditions and attached to the tip of a nylon loop. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3º in a 6º range about ω with the exposure time of 3 seconds per frame. A total of 191 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 13847 strong reflections from the actual data collection. The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of 0.80 Å. A total of 35827 data were harvested by collecting three sets of frames with 0.25º scans in ω with an exposure time 10 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/n$ that yielded chemically reasonable and computationally stable results of refinement.[2] A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms except H included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The Pd-H distance was fixed to be 1.530(2), but the H isotropic displacement coefficient was refined independently. The final least-squares refinement of 531 parameters against 8855 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0301 and 0.0784, respectively. The final difference Fourier map was featureless.

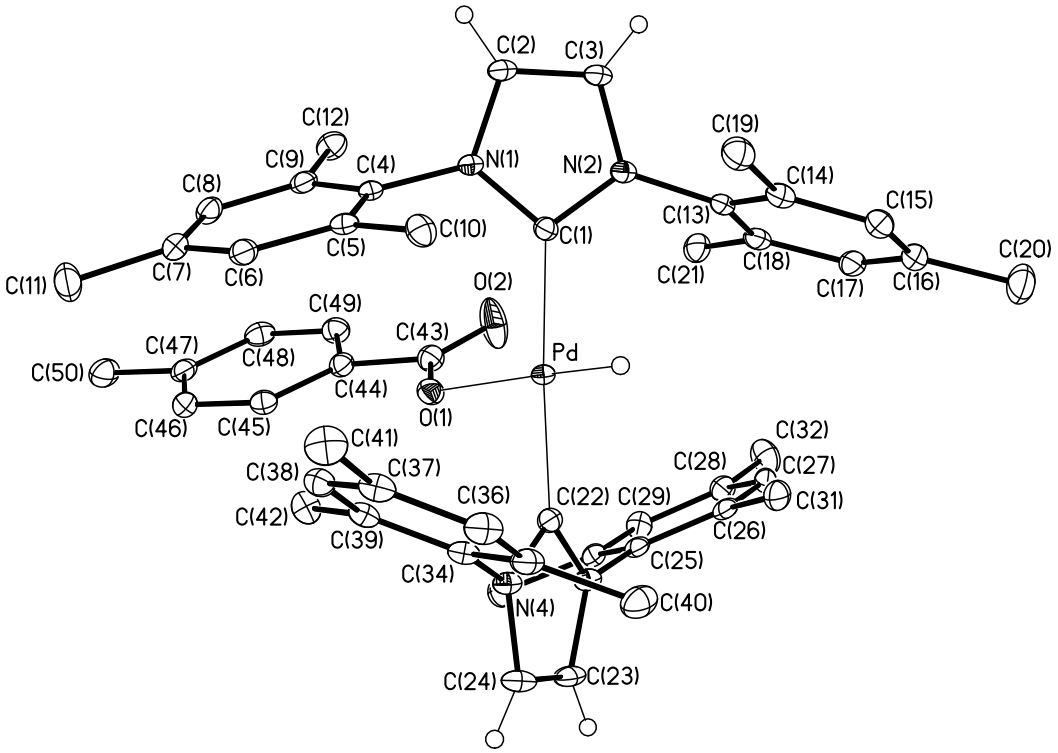

Figure S5. Molecular drawing diagram of $(IMes)_2Pd(H)(O_2CC_6H_4\text{-}p\text{Me})$, **1d**, shown with 30% probability ellipsoids. Most hydrogen atoms are omitted for clarity.

Crystal data and structure refinement for $(IMes)_2Pd(H)(O_2CC_6H_4$-*p*$Me)$, **1d**.

Identification code	stahl26	
Empirical formula	$C_{50}H_{56}N_4O_2Pd$	
Formula weight	851.39	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.8887(4) Å	a= 90°.
	b = 22.7188(8) Å	b= 95.4130(10)°.
	c = 17.5682(6) Å	g = 90°.
Volume	4326.6(3) $Å^3$	
Z	4	
Density (calculated)	1.307 Mg/m^3	
Absorption coefficient	0.473 mm^{-1}	
F(000)	1784	
Crystal size	0.40 x 0.35 x 0.12 mm^3	
Theta range for data collection	1.79 to 26.39°.	
Index ranges	-13<=h<=13, -28<=k<=27, -21<=l<=21	
Reflections collected	35827	
Independent reflections	8855 [R(int) = 0.0397]	
Completeness to theta = 26.39°	99.8 %	
Max. and min. transmission	0.9455 and 0.8334	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8855 / 1 / 531	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0756	
R indices (all data)	R1 = 0.0386, wR2 = 0.0784	
Largest diff. peak and hole	0.771 and -0.334 e.$Å^{-3}$	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for $(IMes)_2Pd(H)(O_2CC_6H_4$-*p*Me), **1d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd	4522(1)	1133(1)	7730(1)	18(1)
O(1)	4505(1)	2034(1)	7394(1)	26(1)
O(2)	4340(2)	1923(1)	6130(1)	56(1)
N(1)	7139(2)	1186(1)	7226(1)	21(1)
N(2)	6154(1)	443(1)	6735(1)	23(1)
N(3)	1831(2)	1353(1)	7958(1)	22(1)
N(4)	2939(1)	1423(1)	9023(1)	22(1)
C(1)	6027(2)	909(1)	7204(1)	20(1)
C(2)	7936(2)	896(1)	6779(1)	26(1)
C(3)	7316(2)	431(1)	6469(1)	27(1)
C(4)	7488(2)	1689(1)	7702(1)	20(1)
C(5)	7620(2)	1612(1)	8496(1)	22(1)
C(6)	7925(2)	2104(1)	8944(1)	24(1)
C(7)	8095(2)	2655(1)	8638(1)	27(1)
C(8)	7985(2)	2706(1)	7843(1)	27(1)
C(9)	7693(2)	2229(1)	7364(1)	23(1)
C(10)	7452(2)	1025(1)	8866(1)	28(1)
C(11)	8374(2)	3181(1)	9151(1)	41(1)
C(12)	7598(2)	2303(1)	6505(1)	30(1)
C(13)	5265(2)	-28(1)	6598(1)	24(1)
C(14)	5432(2)	-531(1)	7056(1)	28(1)
C(15)	4615(2)	-995(1)	6910(1)	32(1)
C(16)	3668(2)	-967(1)	6320(1)	34(1)
C(17)	3534(2)	-463(1)	5889(1)	30(1)
C(18)	4317(2)	25(1)	6015(1)	26(1)
C(19)	6472(2)	-572(1)	7681(1)	35(1)
C(20)	2815(2)	-1491(1)	6167(2)	51(1)
C(21)	4144(2)	576(1)	5546(1)	31(1)
C(22)	3013(2)	1290(1)	8277(1)	20(1)
C(23)	1048(2)	1529(1)	8498(1)	27(1)
C(24)	1744(2)	1574(1)	9163(1)	28(1)
C(25)	1446(2)	1253(1)	7160(1)	21(1)
C(26)	1426(2)	679(1)	6878(1)	24(1)
C(27)	1057(2)	603(1)	6106(1)	26(1)
C(28)	721(2)	1071(1)	5624(1)	27(1)
C(29)	751(2)	1636(1)	5933(1)	27(1)
C(30)	1115(2)	1738(1)	6704(1)	23(1)
C(31)	1822(2)	155(1)	7367(1)	31(1)
C(32)	356(2)	968(1)	4786(1)	42(1)
C(33)	1187(2)	2353(1)	7021(1)	29(1)
C(34)	3941(2)	1343(1)	9611(1)	22(1)
C(35)	3966(2)	819(1)	10029(1)	27(1)
C(36)	4940(2)	741(1)	10591(1)	29(1)
C(37)	5858(2)	1160(1)	10738(1)	27(1)
C(38)	5792(2)	1675(1)	10305(1)	25(1)
C(39)	4836(2)	1776(1)	9731(1)	23(1)
C(40)	2991(2)	356(1)	9863(1)	35(1)
C(41)	6915(2)	1051(1)	11339(1)	35(1)
C(42)	4781(2)	2331(1)	9262(1)	28(1)

C(43)	4500(2)	2216(1)	6714(1)	26(1)
C(44)	4730(2)	2872(1)	6636(1)	24(1)
C(45)	4947(2)	3236(1)	7268(1)	25(1)
C(46)	5187(2)	3832(1)	7182(1)	28(1)
C(47)	5222(2)	4082(1)	6464(1)	28(1)
C(48)	5010(2)	3715(1)	5830(1)	30(1)
C(49)	4778(2)	3121(1)	5916(1)	29(1)
C(50)	5476(2)	4727(1)	6360(1)	40(1)

Bond lengths [Å] and angles [°] for $(IMes)_2Pd(H)(O_2CC_6H_4$-*p*Me) , **1d**.

Pd-C(22)	2.0120(19)	C(19)-H(19C)	0.9600
Pd-C(1)	2.0218(19)	C(20)-H(20A)	0.9600
Pd-O(1)	2.1298(14)	C(20)-H(20B)	0.9600
Pd-H	1.533(2)	C(20)-H(20C)	0.9600
O(1)-C(43)	1.264(2)	C(21)-H(21A)	0.9600
O(2)-C(43)	1.220(2)	C(21)-H(21B)	0.9600
N(1)-C(1)	1.361(2)	C(21)-H(21C)	0.9600
N(1)-C(2)	1.391(2)	C(23)-C(24)	1.336(3)
N(1)-C(4)	1.445(2)	C(23)-H(23)	0.9300
N(2)-C(1)	1.357(2)	C(24)-H(24)	0.9300
N(2)-C(3)	1.390(2)	C(25)-C(30)	1.390(3)
N(2)-C(13)	1.449(2)	C(25)-C(26)	1.395(3)
N(3)-C(22)	1.362(2)	C(26)-C(27)	1.389(3)
N(3)-C(23)	1.392(2)	C(26)-C(31)	1.507(3)
N(3)-C(25)	1.443(3)	C(27)-C(28)	1.387(3)
N(4)-C(22)	1.355(2)	C(27)-H(27)	0.9300
N(4)-C(24)	1.390(2)	C(28)-C(29)	1.394(3)
N(4)-C(34)	1.441(2)	C(28)-C(32)	1.506(3)
C(2)-C(3)	1.340(3)	C(29)-C(30)	1.393(3)
C(2)-H(2)	0.9300	C(29)-H(29)	0.9300
C(3)-H(3)	0.9300	C(30)-C(33)	1.505(3)
C(4)-C(9)	1.390(3)	C(31)-H(31A)	0.9600
C(4)-C(5)	1.400(3)	C(31)-H(31B)	0.9600
C(5)-C(6)	1.391(3)	C(31)-H(31C)	0.9600
C(5)-C(10)	1.502(3)	C(32)-H(32A)	0.9600
C(6)-C(7)	1.380(3)	C(32)-H(32B)	0.9600
C(6)-H(6)	0.9300	C(32)-H(32C)	0.9600
C(7)-C(8)	1.395(3)	C(33)-H(33A)	0.9600
C(7)-C(11)	1.511(3)	C(33)-H(33B)	0.9600
C(8)-C(9)	1.390(3)	C(33)-H(33C)	0.9600
C(8)-H(8)	0.9300	C(34)-C(39)	1.387(3)
C(9)-C(12)	1.514(3)	C(34)-C(35)	1.399(3)
C(10)-H(10A)	0.9600	C(35)-C(36)	1.390(3)
C(10)-H(10B)	0.9600	C(35)-C(40)	1.502(3)
C(10)-H(10C)	0.9600	C(36)-C(37)	1.386(3)
C(11)-H(11A)	0.9600	C(36)-H(36)	0.9300
C(11)-H(11B)	0.9600	C(37)-C(38)	1.394(3)
C(11)-H(11C)	0.9600	C(37)-C(41)	1.508(3)
C(12)-H(12A)	0.9600	C(38)-C(39)	1.399(3)
C(12)-H(12B)	0.9600	C(38)-H(38)	0.9300
C(12)-H(12C)	0.9600	C(39)-C(42)	1.504(3)
C(13)-C(18)	1.390(3)	C(40)-H(40A)	0.9600
C(13)-C(14)	1.399(3)	C(40)-H(40B)	0.9600
C(14)-C(15)	1.387(3)	C(40)-H(40C)	0.9600
C(14)-C(19)	1.505(3)	C(41)-H(41A)	0.9600
C(15)-C(16)	1.394(3)	C(41)-H(41B)	0.9600
C(15)-H(15)	0.9300	C(41)-H(41C)	0.9600
C(16)-C(17)	1.373(3)	C(42)-H(42A)	0.9600
C(16)-C(20)	1.519(3)	C(42)-H(42B)	0.9600
C(17)-C(18)	1.403(3)	C(42)-H(42C)	0.9600
C(17)-H(17)	0.9300	C(44)-C(45)	1.386(3)
C(18)-C(21)	1.500(3)	C(44)-C(49)	1.392(3)
C(19)-H(19A)	0.9600	C(45)-C(46)	1.389(3)
C(19)-H(19B)	0.9600	C(45)-H(45)	0.9300

C(46)-C(47)	1.388(3)	C(48)-H(48)	0.9300
C(46)-H(46)	0.9300	C(49)-H(49)	0.9300
C(47)-C(48)	1.393(3)	C(50)-H(50A)	0.9600
C(47)-C(50)	1.505(3)	C(50)-H(50B)	0.9600
C(48)-C(49)	1.384(3)	C(50)-H(50C)	0.9600
C(22)-Pd-C(1)	175.52(7)	H(10B)-C(10)-H(10C)	109.5
C(22)-Pd-O(1)	88.66(6)	C(7)-C(11)-H(11A)	109.5
C(1)-Pd-O(1)	95.81(7)	C(7)-C(11)-H(11B)	109.5
C(22)-Pd-H	89.2(6)	H(11A)-C(11)-H(11B)	109.5
C(1)-Pd-H	86.4(6)	C(7)-C(11)-H(11C)	109.5
O(1)-Pd-H	172.8(7)	H(11A)-C(11)-H(11C)	109.5
C(43)-O(1)-Pd	125.15(13)	H(11B)-C(11)-H(11C)	109.5
C(1)-N(1)-C(2)	111.37(16)	C(9)-C(12)-H(12A)	109.5
C(1)-N(1)-C(4)	124.54(16)	C(9)-C(12)-H(12B)	109.5
C(2)-N(1)-C(4)	123.90(16)	H(12A)-C(12)-H(12B)	109.5
C(1)-N(2)-C(3)	111.56(16)	C(9)-C(12)-H(12C)	109.5
C(1)-N(2)-C(13)	124.95(16)	H(12A)-C(12)-H(12C)	109.5
C(3)-N(2)-C(13)	123.06(16)	H(12B)-C(12)-H(12C)	109.5
C(22)-N(3)-C(23)	111.48(17)	C(18)-C(13)-C(14)	122.82(19)
C(22)-N(3)-C(25)	124.01(16)	C(18)-C(13)-N(2)	119.75(19)
C(23)-N(3)-C(25)	124.51(16)	C(14)-C(13)-N(2)	117.40(18)
C(22)-N(4)-C(24)	111.63(16)	C(15)-C(14)-C(13)	117.9(2)
C(22)-N(4)-C(34)	123.69(16)	C(15)-C(14)-C(19)	120.9(2)
C(24)-N(4)-C(34)	124.23(16)	C(13)-C(14)-C(19)	121.17(19)
N(2)-C(1)-N(1)	103.74(16)	C(14)-C(15)-C(16)	121.2(2)
N(2)-C(1)-Pd	127.44(14)	C(14)-C(15)-H(15)	119.4
N(1)-C(1)-Pd	128.82(14)	C(16)-C(15)-H(15)	119.4
C(3)-C(2)-N(1)	106.63(18)	C(17)-C(16)-C(15)	118.8(2)
C(3)-C(2)-H(2)	126.7	C(17)-C(16)-C(20)	121.7(2)
N(1)-C(2)-H(2)	126.7	C(15)-C(16)-C(20)	119.5(2)
C(2)-C(3)-N(2)	106.70(17)	C(16)-C(17)-C(18)	122.8(2)
C(2)-C(3)-H(3)	126.6	C(16)-C(17)-H(17)	118.6
N(2)-C(3)-H(3)	126.6	C(18)-C(17)-H(17)	118.6
C(9)-C(4)-C(5)	122.02(18)	C(13)-C(18)-C(17)	116.4(2)
C(9)-C(4)-N(1)	119.74(17)	C(13)-C(18)-C(21)	121.59(19)
C(5)-C(4)-N(1)	118.24(17)	C(17)-C(18)-C(21)	121.99(19)
C(6)-C(5)-C(4)	117.39(18)	C(14)-C(19)-H(19A)	109.5
C(6)-C(5)-C(10)	120.11(18)	C(14)-C(19)-H(19B)	109.5
C(4)-C(5)-C(10)	122.50(18)	H(19A)-C(19)-H(19B)	109.5
C(7)-C(6)-C(5)	122.80(19)	C(14)-C(19)-H(19C)	109.5
C(7)-C(6)-H(6)	118.6	H(19A)-C(19)-H(19C)	109.5
C(5)-C(6)-H(6)	118.6	H(19B)-C(19)-H(19C)	109.5
C(6)-C(7)-C(8)	117.62(19)	C(16)-C(20)-H(20A)	109.5
C(6)-C(7)-C(11)	120.8(2)	C(16)-C(20)-H(20B)	109.5
C(8)-C(7)-C(11)	121.6(2)	H(20A)-C(20)-H(20B)	109.5
C(9)-C(8)-C(7)	122.27(19)	C(16)-C(20)-H(20C)	109.5
C(9)-C(8)-H(8)	118.9	H(20A)-C(20)-H(20C)	109.5
C(7)-C(8)-H(8)	118.9	H(20B)-C(20)-H(20C)	109.5
C(8)-C(9)-C(4)	117.83(18)	C(18)-C(21)-H(21A)	109.5
C(8)-C(9)-C(12)	120.55(19)	C(18)-C(21)-H(21B)	109.5
C(4)-C(9)-C(12)	121.62(18)	H(21A)-C(21)-H(21B)	109.5
C(5)-C(10)-H(10A)	109.5	C(18)-C(21)-H(21C)	109.5
C(5)-C(10)-H(10B)	109.5	H(21A)-C(21)-H(21C)	109.5
H(10A)-C(10)-H(10B)	109.5	H(21B)-C(21)-H(21C)	109.5
C(5)-C(10)-H(10C)	109.5	N(4)-C(22)-N(3)	103.53(16)
H(10A)-C(10)-H(10C)	109.5	N(4)-C(22)-Pd	128.83(14)

N(3)-C(22)-Pd	127.25(14)
C(24)-C(23)-N(3)	106.54(17)
C(24)-C(23)-H(23)	126.7
N(3)-C(23)-H(23)	126.7
C(23)-C(24)-N(4)	106.81(17)
C(23)-C(24)-H(24)	126.6
N(4)-C(24)-H(24)	126.6
C(30)-C(25)-C(26)	122.82(19)
C(30)-C(25)-N(3)	118.14(17)
C(26)-C(25)-N(3)	119.04(18)
C(27)-C(26)-C(25)	117.11(19)
C(27)-C(26)-C(31)	120.00(19)
C(25)-C(26)-C(31)	122.86(19)
C(28)-C(27)-C(26)	122.49(19)
C(28)-C(27)-H(27)	118.8
C(26)-C(27)-H(27)	118.8
C(27)-C(28)-C(29)	118.25(19)
C(27)-C(28)-C(32)	120.48(19)
C(29)-C(28)-C(32)	121.3(2)
C(30)-C(29)-C(28)	121.68(19)
C(30)-C(29)-H(29)	119.2
C(28)-C(29)-H(29)	119.2
C(25)-C(30)-C(29)	117.65(18)
C(25)-C(30)-C(33)	121.39(18)
C(29)-C(30)-C(33)	120.93(19)
C(26)-C(31)-H(31A)	109.5
C(26)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(26)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(28)-C(32)-H(32A)	109.5
C(28)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(28)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(30)-C(33)-H(33A)	109.5
C(30)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(30)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(39)-C(34)-C(35)	123.05(18)
C(39)-C(34)-N(4)	119.60(17)
C(35)-C(34)-N(4)	117.34(18)
C(36)-C(35)-C(34)	117.19(19)
C(36)-C(35)-C(40)	121.80(19)
C(34)-C(35)-C(40)	121.00(19)
C(37)-C(36)-C(35)	122.25(19)
C(37)-C(36)-H(36)	118.9
C(35)-C(36)-H(36)	118.9
C(36)-C(37)-C(38)	118.39(19)
C(36)-C(37)-C(41)	120.53(19)
C(38)-C(37)-C(41)	121.1(2)
C(37)-C(38)-C(39)	121.9(2)
C(37)-C(38)-H(38)	119.1
C(39)-C(38)-H(38)	119.1
C(34)-C(39)-C(38)	117.22(18)
C(34)-C(39)-C(42)	121.35(18)
C(38)-C(39)-C(42)	121.43(19)
C(35)-C(40)-H(40A)	109.5
C(35)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(35)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(37)-C(41)-H(41A)	109.5
C(37)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(37)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(39)-C(42)-H(42A)	109.5
C(39)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(39)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
O(2)-C(43)-O(1)	127.1(2)
O(2)-C(43)-C(44)	118.10(19)
O(1)-C(43)-C(44)	114.77(18)
C(45)-C(44)-C(49)	117.79(19)
C(45)-C(44)-C(43)	122.10(18)
C(49)-C(44)-C(43)	120.06(18)
C(44)-C(45)-C(46)	121.01(19)
C(44)-C(45)-H(45)	119.5
C(46)-C(45)-H(45)	119.5
C(47)-C(46)-C(45)	121.2(2)
C(47)-C(46)-H(46)	119.4
C(45)-C(46)-H(46)	119.4
C(46)-C(47)-C(48)	117.7(2)
C(46)-C(47)-C(50)	122.0(2)
C(48)-C(47)-C(50)	120.3(2)
C(49)-C(48)-C(47)	121.1(2)
C(49)-C(48)-H(48)	119.5
C(47)-C(48)-H(48)	119.5
C(48)-C(49)-C(44)	121.2(2)
C(48)-C(49)-H(49)	119.4
C(44)-C(49)-H(49)	119.4
C(47)-C(50)-H(50A)	109.5
C(47)-C(50)-H(50B)	109.5
H(50A)-C(50)-H(50B)	109.5
C(47)-C(50)-H(50C)	109.5
H(50A)-C(50)-H(50C)	109.5
H(50B)-C(50)-H(50C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $(IMes)_2Pd(H)(O_2CC_6H_4\text{-}p\text{Me})$, **1d**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd	14(1)	19(1)	21(1)	-1(1)	3(1)	1(1)
O(1)	29(1)	22(1)	28(1)	0(1)	7(1)	1(1)
O(2)	108(2)	35(1)	23(1)	-5(1)	1(1)	-19(1)
N(1)	16(1)	24(1)	25(1)	-4(1)	6(1)	0(1)
N(2)	18(1)	26(1)	27(1)	-6(1)	5(1)	1(1)
N(3)	17(1)	25(1)	24(1)	2(1)	5(1)	2(1)
N(4)	18(1)	24(1)	23(1)	2(1)	6(1)	3(1)
C(1)	19(1)	20(1)	21(1)	-3(1)	1(1)	2(1)
C(2)	17(1)	31(1)	31(1)	-5(1)	8(1)	2(1)
C(3)	20(1)	31(1)	32(1)	-9(1)	9(1)	1(1)
C(4)	12(1)	22(1)	27(1)	-5(1)	3(1)	2(1)
C(5)	14(1)	25(1)	28(1)	-1(1)	4(1)	3(1)
C(6)	20(1)	31(1)	23(1)	-3(1)	3(1)	-2(1)
C(7)	21(1)	28(1)	33(1)	-6(1)	5(1)	-5(1)
C(8)	22(1)	23(1)	35(1)	2(1)	6(1)	-5(1)
C(9)	15(1)	29(1)	26(1)	-1(1)	4(1)	-1(1)
C(10)	31(1)	23(1)	29(1)	1(1)	0(1)	4(1)
C(11)	51(2)	32(1)	40(1)	-11(1)	9(1)	-12(1)
C(12)	27(1)	36(1)	27(1)	3(1)	3(1)	-2(1)
C(13)	19(1)	24(1)	31(1)	-11(1)	8(1)	0(1)
C(14)	23(1)	26(1)	36(1)	-5(1)	6(1)	5(1)
C(15)	28(1)	22(1)	48(1)	-1(1)	8(1)	3(1)
C(16)	24(1)	26(1)	54(2)	-9(1)	8(1)	-1(1)
C(17)	20(1)	33(1)	36(1)	-12(1)	2(1)	-2(1)
C(18)	22(1)	29(1)	27(1)	-8(1)	8(1)	2(1)
C(19)	32(1)	30(1)	42(1)	-1(1)	1(1)	4(1)
C(20)	34(1)	33(1)	83(2)	-4(1)	-4(1)	-8(1)
C(21)	28(1)	34(1)	30(1)	-5(1)	0(1)	-5(1)
C(22)	19(1)	18(1)	25(1)	2(1)	3(1)	1(1)
C(23)	18(1)	31(1)	33(1)	3(1)	10(1)	6(1)
C(24)	24(1)	34(1)	27(1)	3(1)	11(1)	8(1)
C(25)	12(1)	25(1)	26(1)	0(1)	4(1)	-1(1)
C(26)	14(1)	25(1)	34(1)	1(1)	6(1)	-2(1)
C(27)	20(1)	21(1)	39(1)	-7(1)	3(1)	-2(1)
C(28)	20(1)	31(1)	31(1)	-4(1)	-1(1)	-1(1)
C(29)	25(1)	25(1)	29(1)	3(1)	-3(1)	1(1)
C(30)	16(1)	25(1)	30(1)	-3(1)	2(1)	-2(1)
C(31)	31(1)	21(1)	41(1)	3(1)	7(1)	-1(1)
C(32)	45(2)	40(1)	40(1)	-10(1)	-12(1)	4(1)
C(33)	31(1)	24(1)	30(1)	0(1)	-1(1)	1(1)
C(34)	21(1)	27(1)	20(1)	1(1)	6(1)	7(1)
C(35)	25(1)	27(1)	30(1)	2(1)	10(1)	5(1)
C(36)	32(1)	28(1)	28(1)	10(1)	8(1)	8(1)
C(37)	26(1)	32(1)	22(1)	1(1)	5(1)	8(1)
C(38)	26(1)	27(1)	22(1)	-2(1)	4(1)	2(1)
C(39)	26(1)	24(1)	19(1)	-1(1)	7(1)	6(1)
C(40)	29(1)	31(1)	45(1)	10(1)	9(1)	3(1)
C(41)	33(1)	39(1)	32(1)	8(1)	-2(1)	7(1)

C(42)	33(1)	25(1)	25(1)	0(1)	-1(1)	3(1)
C(43)	24(1)	28(1)	27(1)	-1(1)	1(1)	0(1)
C(44)	20(1)	25(1)	27(1)	0(1)	1(1)	-1(1)
C(45)	22(1)	27(1)	25(1)	1(1)	2(1)	2(1)
C(46)	23(1)	28(1)	33(1)	-5(1)	2(1)	-1(1)
C(47)	19(1)	26(1)	41(1)	2(1)	6(1)	-1(1)
C(48)	26(1)	35(1)	31(1)	7(1)	8(1)	2(1)
C(49)	28(1)	34(1)	25(1)	-1(1)	3(1)	0(1)
C(50)	37(1)	32(1)	53(2)	5(1)	14(1)	-4(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for $(IMes)_2Pd(H)(O_2CC_6H_4$-*p*Me), **1d**.

	x	y	z	U(eq)
H	4590(16)	513(3)	8074(9)	13(5)
H(2)	8742	1003	6709	31
H(3)	7607	155	6139	32
H(6)	8019	2061	9473	29
H(8)	8112	3072	7626	32
H(10A)	7856	1028	9375	42
H(10B)	7805	722	8573	42
H(10C)	6588	949	8884	42
H(11A)	8055	3115	9634	61
H(11B)	7995	3526	8915	61
H(11C)	9251	3238	9229	61
H(12A)	7523	2713	6379	45
H(12B)	6885	2096	6280	45
H(12C)	8325	2146	6310	45
H(15)	4701	-1331	7213	39
H(17)	2897	-444	5498	36
H(19A)	6346	-906	7999	52
H(19B)	6496	-220	7985	52
H(19C)	7239	-616	7458	52
H(20A)	2170	-1476	6503	76
H(20B)	3277	-1849	6256	76
H(20C)	2460	-1481	5646	76
H(21A)	3930	895	5866	46
H(21B)	3494	517	5144	46
H(21C)	4896	668	5327	46
H(23)	206	1601	8412	32
H(24)	1480	1685	9631	33
H(27)	1034	224	5905	32
H(29)	523	1954	5617	32
H(31A)	1439	-195	7148	46
H(31B)	1578	211	7873	46
H(31C)	2703	114	7392	46
H(32A)	894	679	4596	64
H(32B)	421	1330	4511	64
H(32C)	-479	828	4718	64
H(33A)	646	2389	7419	43
H(33B)	944	2629	6621	43
H(33C)	2019	2435	7225	43
H(36)	4977	396	10878	35
H(38)	6402	1959	10400	30
H(40A)	3201	13	10166	52
H(40B)	2941	254	9331	52
H(40C)	2209	506	9985	52
H(41A)	6645	800	11730	52
H(41B)	7194	1419	11561	52
H(41C)	7579	864	11109	52
H(42A)	4730	2232	8729	41
H(42B)	5511	2560	9394	41
H(42C)	4068	2556	9364	41
H(45)	4932	3080	7756	29

H(46)	5328	4068	7615	33
H(48)	5024	3872	5342	36
H(49)	4653	2884	5484	35
H(50A)	5573	4917	6851	60
H(50B)	4799	4903	6052	60
H(50C)	6218	4773	6112	60

Torsion angles [°] for $(IMes)_2Pd(H)(O_2CC_6H_4$-*p*Me), **1d**.

C(22)-Pd-O(1)-C(43)	-125.63(16)
C(1)-Pd-O(1)-C(43)	54.07(16)
C(3)-N(2)-C(1)-N(1)	-0.2(2)
C(13)-N(2)-C(1)-N(1)	172.36(18)
C(3)-N(2)-C(1)-Pd	179.26(14)
C(13)-N(2)-C(1)-Pd	-8.1(3)
C(2)-N(1)-C(1)-N(2)	0.0(2)
C(4)-N(1)-C(1)-N(2)	-175.25(17)
C(2)-N(1)-C(1)-Pd	-179.50(14)
C(4)-N(1)-C(1)-Pd	5.2(3)
C(22)-Pd-C(1)-N(2)	45.2(10)
O(1)-Pd-C(1)-N(2)	-131.02(17)
C(22)-Pd-C(1)-N(1)	-135.4(9)
O(1)-Pd-C(1)-N(1)	48.37(18)
C(1)-N(1)-C(2)-C(3)	0.2(2)
C(4)-N(1)-C(2)-C(3)	175.53(18)
N(1)-C(2)-C(3)-N(2)	-0.4(2)
C(1)-N(2)-C(3)-C(2)	0.4(2)
C(13)-N(2)-C(3)-C(2)	-172.37(18)
C(1)-N(1)-C(4)-C(9)	-114.1(2)
C(2)-N(1)-C(4)-C(9)	71.2(2)
C(1)-N(1)-C(4)-C(5)	66.5(2)
C(2)-N(1)-C(4)-C(5)	-108.2(2)
C(9)-C(4)-C(5)-C(6)	2.2(3)
N(1)-C(4)-C(5)-C(6)	-178.42(16)
C(9)-C(4)-C(5)-C(10)	-177.39(18)
N(1)-C(4)-C(5)-C(10)	2.0(3)
C(4)-C(5)-C(6)-C(7)	0.2(3)
C(10)-C(5)-C(6)-C(7)	179.78(19)
C(5)-C(6)-C(7)-C(8)	-1.8(3)
C(5)-C(6)-C(7)-C(11)	177.42(19)
C(6)-C(7)-C(8)-C(9)	1.2(3)
C(11)-C(7)-C(8)-C(9)	-178.0(2)
C(7)-C(8)-C(9)-C(4)	1.0(3)
C(7)-C(8)-C(9)-C(12)	-179.26(19)
C(5)-C(4)-C(9)-C(8)	-2.8(3)
N(1)-C(4)-C(9)-C(8)	177.85(16)
C(5)-C(4)-C(9)-C(12)	177.51(18)
N(1)-C(4)-C(9)-C(12)	-1.9(3)
C(1)-N(2)-C(13)-C(18)	88.8(2)
C(3)-N(2)-C(13)-C(18)	-99.5(2)
C(1)-N(2)-C(13)-C(14)	-93.1(2)
C(3)-N(2)-C(13)-C(14)	78.6(2)
C(18)-C(13)-C(14)-C(15)	0.6(3)
N(2)-C(13)-C(14)-C(15)	-177.48(18)
C(18)-C(13)-C(14)-C(19)	179.86(19)
N(2)-C(13)-C(14)-C(19)	1.8(3)
C(13)-C(14)-C(15)-C(16)	1.0(3)
C(19)-C(14)-C(15)-C(16)	-178.4(2)
C(14)-C(15)-C(16)-C(17)	-1.4(3)
C(14)-C(15)-C(16)-C(20)	178.4(2)
C(15)-C(16)-C(17)-C(18)	0.5(3)
C(20)-C(16)-C(17)-C(18)	-179.4(2)

C(14)-C(13)-C(18)-C(17)	-1.5(3)
N(2)-C(13)-C(18)-C(17)	176.52(17)
C(14)-C(13)-C(18)-C(21)	178.51(19)
N(2)-C(13)-C(18)-C(21)	-3.5(3)
C(16)-C(17)-C(18)-C(13)	1.0(3)
C(16)-C(17)-C(18)-C(21)	-179.0(2)
C(24)-N(4)-C(22)-N(3)	-0.9(2)
C(34)-N(4)-C(22)-N(3)	171.69(17)
C(24)-N(4)-C(22)-Pd	172.29(14)
C(34)-N(4)-C(22)-Pd	-15.1(3)
C(23)-N(3)-C(22)-N(4)	0.7(2)
C(25)-N(3)-C(22)-N(4)	-179.63(16)
C(23)-N(3)-C(22)-Pd	-172.60(14)
C(25)-N(3)-C(22)-Pd	7.1(3)
C(1)-Pd-C(22)-N(4)	88.7(10)
O(1)-Pd-C(22)-N(4)	-95.09(18)
C(1)-Pd-C(22)-N(3)	-99.7(10)
O(1)-Pd-C(22)-N(3)	76.55(17)
C(22)-N(3)-C(23)-C(24)	-0.3(2)
C(25)-N(3)-C(23)-C(24)	-179.95(18)
N(3)-C(23)-C(24)-N(4)	-0.3(2)
C(22)-N(4)-C(24)-C(23)	0.7(2)
C(34)-N(4)-C(24)-C(23)	-171.78(18)
C(22)-N(3)-C(25)-C(30)	-109.3(2)
C(23)-N(3)-C(25)-C(30)	70.4(2)
C(22)-N(3)-C(25)-C(26)	70.5(2)
C(23)-N(3)-C(25)-C(26)	-109.9(2)
C(30)-C(25)-C(26)-C(27)	0.1(3)
N(3)-C(25)-C(26)-C(27)	-179.64(17)
C(30)-C(25)-C(26)-C(31)	178.10(18)
N(3)-C(25)-C(26)-C(31)	-1.6(3)
C(25)-C(26)-C(27)-C(28)	0.1(3)
C(31)-C(26)-C(27)-C(28)	-177.92(19)
C(26)-C(27)-C(28)-C(29)	-0.4(3)
C(26)-C(27)-C(28)-C(32)	178.5(2)
C(27)-C(28)-C(29)-C(30)	0.4(3)
C(32)-C(28)-C(29)-C(30)	-178.5(2)
C(26)-C(25)-C(30)-C(29)	-0.1(3)
N(3)-C(25)-C(30)-C(29)	179.66(17)
C(26)-C(25)-C(30)-C(33)	-177.92(18)
N(3)-C(25)-C(30)-C(33)	1.8(3)
C(28)-C(29)-C(30)-C(25)	-0.2(3)
C(28)-C(29)-C(30)-C(33)	177.68(19)
C(22)-N(4)-C(34)-C(39)	84.2(2)
C(24)-N(4)-C(34)-C(39)	-104.1(2)
C(22)-N(4)-C(34)-C(35)	-94.9(2)
C(24)-N(4)-C(34)-C(35)	76.7(2)
C(39)-C(34)-C(35)-C(36)	0.3(3)
N(4)-C(34)-C(35)-C(36)	179.44(17)
C(39)-C(34)-C(35)-C(40)	-178.41(19)
N(4)-C(34)-C(35)-C(40)	0.7(3)
C(34)-C(35)-C(36)-C(37)	-0.1(3)
C(40)-C(35)-C(36)-C(37)	178.6(2)
C(35)-C(36)-C(37)-C(38)	0.1(3)
C(35)-C(36)-C(37)-C(41)	-178.5(2)
C(36)-C(37)-C(38)-C(39)	-0.2(3)

C(41)-C(37)-C(38)-C(39)	178.30(19)
C(35)-C(34)-C(39)-C(38)	-0.4(3)
N(4)-C(34)-C(39)-C(38)	-179.56(16)
C(35)-C(34)-C(39)-C(42)	179.32(18)
N(4)-C(34)-C(39)-C(42)	0.2(3)
C(37)-C(38)-C(39)-C(34)	0.4(3)
C(37)-C(38)-C(39)-C(42)	-179.38(18)
Pd-O(1)-C(43)-O(2)	10.5(3)
Pd-O(1)-C(43)-C(44)	-169.00(12)
O(2)-C(43)-C(44)-C(45)	-178.6(2)
O(1)-C(43)-C(44)-C(45)	1.0(3)
O(2)-C(43)-C(44)-C(49)	-1.3(3)
O(1)-C(43)-C(44)-C(49)	178.30(18)
C(49)-C(44)-C(45)-C(46)	0.9(3)
C(43)-C(44)-C(45)-C(46)	178.30(19)
C(44)-C(45)-C(46)-C(47)	-0.2(3)
C(45)-C(46)-C(47)-C(48)	-0.2(3)
C(45)-C(46)-C(47)-C(50)	179.8(2)
C(46)-C(47)-C(48)-C(49)	-0.2(3)
C(50)-C(47)-C(48)-C(49)	179.8(2)
C(47)-C(48)-C(49)-C(44)	1.0(3)
C(45)-C(44)-C(49)-C(48)	-1.3(3)
C(43)-C(44)-C(49)-C(48)	-178.77(19)
C(44)-Pd-C(1)-N(1)	54.53(17)
C(44)-Pd-C(22)-N(3)	70.31(17)

Selected dihedral angles [°] between planes for $(IMes)_2Pd(H)(O_2CC_6H_4$-*p*Me) , **1d**.

Plane	Plane	Angle
C(1) N(1) C(2) C(3) N(2)	C(4)…C(9)	68.87(8)
C(1) N(1) C(2) C(3) N(2)	C(13)…C(18)	83.44(8)
C(22) N(3) C(4) C(23) N(24)	C(25)…C(30)	70.30(8)
C(22) N(3) C(4) C(23) N(24)	C(34)…C(39)	80.73(7)
C(1) N(1) C(2) C(3) N(2)	C(22) N(3) C(4) C(23) N(24)	50.63(8)
C(43) O(1) O(2)	C(44)…C(49)	1.86(16)

[1] Konnick, M. M.; Stahl, S. S. *J. Am. Chem. Soc.* **2008,** *130*, 5753-5762.

[2] Bruker-AXS. (2000-2001) SADABS V.2.03, SAINT V.6.22, SHELXTL V.6.10
& SMART 5.622 Software Reference Manuals. Bruker-AXS, Madison, Wisconsin, USA.