Electronic Supplementary Information

C-O bond scission of methoxide on Pd nanoparticles: A density functional study

Ilya V. Yudanov,[a,b] Konstantin M. Neyman,[c] Notker Rösch[*a]

[a] *Department Chemie, Technische Universität München, 85747 Garching, Germany*
[b] *Boreskov Institute of Catalysis, 630090 Novosibirsk, Russia*
[c] *Institució Catalana de Recerca i Estudis Avançats (ICREA), 08010 Barcelona and Departament de Química Física, Universitat de Barcelona, 08028 Barcelona, Spain*

[*] Corresponding author. E-mail address: roesch@ch.tum.de

Table S1. Cartesian coordinates (Å) of all atoms of the cluster Pd_{79} with bulk-terminated geometry (model **B**). Symmetry restrictions according to point group O_h.

	X	Y	Z
Pd	0.00000	0.00000	0.00000
Pd	1.94454	1.94454	0.00000
Pd	-1.94454	1.94454	0.00000
Pd	1.94454	-1.94454	0.00000
Pd	-1.94454	-1.94454	0.00000
Pd	0.00000	1.94454	1.94454
Pd	-1.94454	0.00000	1.94454
Pd	1.94454	0.00000	1.94454
Pd	0.00000	-1.94454	1.94454
Pd	0.00000	-1.94454	-1.94454
Pd	0.00000	1.94454	-1.94454
Pd	1.94454	0.00000	-1.94454
Pd	-1.94454	0.00000	-1.94454
Pd	0.00000	0.00000	3.88909
Pd	0.00000	0.00000	-3.88909
Pd	3.88909	0.00000	0.00000
Pd	0.00000	3.88909	0.00000
Pd	0.00000	-3.88909	0.00000
Pd	-3.88909	0.00000	0.00000
Pd	3.88909	1.94454	1.94454
Pd	-1.94454	3.88909	1.94454
Pd	1.94454	-3.88909	1.94454
Pd	-3.88909	-1.94454	1.94454
Pd	3.88909	-1.94454	-1.94454
Pd	-3.88909	1.94454	-1.94454
Pd	1.94454	3.88909	-1.94454
Pd	-1.94454	-3.88909	-1.94454
Pd	1.94454	3.88909	1.94454
Pd	-3.88909	1.94454	1.94454
Pd	3.88909	-1.94454	1.94454
Pd	-1.94454	-3.88909	1.94454
Pd	1.94454	-3.88909	-1.94454
Pd	-1.94454	3.88909	-1.94454
Pd	3.88909	1.94454	-1.94454
Pd	-3.88909	-1.94454	-1.94454
Pd	1.94454	1.94454	3.88909
Pd	-1.94454	1.94454	3.88909
Pd	1.94454	-1.94454	3.88909
Pd	-1.94454	-1.94454	3.88909
Pd	1.94454	-1.94454	-3.88909
Pd	-1.94454	1.94454	-3.88909
Pd	1.94454	1.94454	-3.88909
Pd	-1.94454	-1.94454	-3.88909
Pd	3.88909	3.88909	0.00000
Pd	-3.88909	3.88909	0.00000
Pd	3.88909	-3.88909	0.00000
Pd	-3.88909	-3.88909	0.00000
Pd	0.00000	3.88909	3.88909
Pd	-3.88909	0.00000	3.88909
Pd	3.88909	0.00000	3.88909
Pd	0.00000	-3.88909	3.88909
Pd	0.00000	-3.88909	-3.88909

Pd	0.00000	3.88909	-3.88909
Pd	3.88909	0.00000	-3.88909
Pd	-3.88909	0.00000	-3.88909
Pd	5.83363	1.94454	0.00000
Pd	-1.94454	5.83363	0.00000
Pd	1.94454	-5.83363	0.00000
Pd	-5.83363	-1.94454	0.00000
Pd	5.83363	-1.94454	0.00000
Pd	-5.83363	1.94454	0.00000
Pd	1.94454	5.83363	0.00000
Pd	-1.94454	-5.83363	0.00000
Pd	5.83363	0.00000	1.94454
Pd	0.00000	5.83363	1.94454
Pd	0.00000	-5.83363	1.94454
Pd	-5.83363	0.00000	1.94454
Pd	5.83363	0.00000	-1.94454
Pd	-5.83363	0.00000	-1.94454
Pd	0.00000	5.83363	-1.94454
Pd	0.00000	-5.83363	-1.94454
Pd	0.00000	1.94454	5.83363
Pd	-1.94454	0.00000	5.83363
Pd	1.94454	0.00000	5.83363
Pd	0.00000	-1.94454	5.83363
Pd	0.00000	-1.94454	-5.83363
Pd	0.00000	1.94454	-5.83363
Pd	1.94454	0.00000	-5.83363
Pd	-1.94454	0.00000	-5.83363

Table S2. Cartesian coordinates (Å) of all atoms of the cluster Pd_{79} (model **B,** Table S1) with adsorbed CH_3O. Symmetry restrictions according to point group O_h.

	X	Y	Z
O	3.49657	3.49657	3.49657
O	3.49657	-3.49657	-3.49657
O	-3.49657	3.49657	-3.49657
O	-3.49657	-3.49657	3.49657
O	3.49657	-3.49657	3.49657
O	3.49657	3.49657	-3.49657
O	-3.49657	3.49657	3.49657
O	-3.49657	-3.49657	-3.49657
C	4.31877	4.31877	4.31877
C	4.31877	-4.31877	-4.31877
C	-4.31877	4.31877	-4.31877
C	-4.31877	-4.31877	4.31877
C	4.31877	-4.31877	4.31877
C	4.31877	4.31877	-4.31877
C	-4.31877	4.31877	4.31877
C	-4.31877	-4.31877	-4.31877
H	3.68362	4.95880	4.95880
H	3.68362	-4.95880	-4.95880
H	-3.68362	4.95880	-4.95880
H	-3.68362	-4.95880	4.95880
H	4.95880	3.68362	4.95880
H	-4.95880	3.68362	-4.95880
H	-4.95880	-3.68362	4.95880
H	4.95880	-3.68362	-4.95880
H	4.95880	4.95880	3.68362
H	4.95880	-4.95880	-3.68362
H	-4.95880	4.95880	-3.68362
H	-4.95880	-4.95880	3.68362
H	3.68362	-4.95880	4.95880
H	4.95880	4.95880	-3.68362
H	-4.95880	3.68362	4.95880
H	3.68362	4.95880	-4.95880
H	-4.95880	4.95880	3.68362
H	4.95880	-3.68362	4.95880
H	4.95880	3.68362	-4.95880
H	-4.95880	-3.68362	-4.95880
H	4.95880	-4.95880	3.68362
H	-3.68362	4.95880	4.95880
H	-4.95880	-4.95880	-3.68362
H	-3.68362	-4.95880	-4.95880

Table S3. Cartesian coordinates (Å) of all atoms of the cluster Pd_{79} (model **B,** Table S1) with the adsorbates O (fcc position on the (111) facet) and CH_3 (on-top, edge). Symmetry restrictions according to point group D_{4h}.

	X	Y	Z
C	0.00000	5.32233	5.32233
C	-5.32233	0.00000	5.32233
C	5.32233	0.00000	5.32233
C	0.00000	-5.32233	5.32233
C	0.00000	-5.32233	-5.32233
C	0.00000	5.32233	-5.32233
C	5.32233	0.00000	-5.32233
C	-5.32233	0.00000	-5.32233
H	0.00000	6.28833	4.79426
H	-6.28833	0.00000	4.79426
H	6.28833	0.00000	4.79426
H	0.00000	-6.28833	4.79426
H	0.00000	-6.28833	-4.79426
H	0.00000	6.28833	-4.79426
H	6.28833	0.00000	-4.79426
H	-6.28833	0.00000	-4.79426
H	0.91141	5.20794	5.92094
H	-5.20794	0.91141	5.92094
H	5.20794	-0.91141	5.92094
H	-0.91141	-5.20794	5.92094
H	0.91141	-5.20794	-5.92094
H	-0.91141	5.20794	-5.92094
H	5.20794	0.91141	-5.92094
H	-5.20794	-0.91141	-5.92094
H	-0.91141	-5.20794	-5.92094
H	5.20794	-0.91141	-5.92094
H	-5.20794	0.91141	-5.92094
H	0.91141	5.20794	-5.92094
H	-0.91141	5.20794	5.92094
H	0.91141	-5.20794	5.92094
H	-5.20794	-0.91141	5.92094
H	5.20794	0.91141	5.92094
O	3.27844	3.27844	3.27844
O	-3.27844	3.27844	3.27844
O	3.27844	-3.27844	3.27844
O	-3.27844	-3.27844	3.27844
O	3.27844	-3.27844	-3.27844
O	-3.27844	3.27844	-3.27844
O	3.27844	3.27844	-3.27844
O	-3.27844	-3.27844	-3.27844

Table S4. Cartesian coordinates (Å) of all atoms of the cluster Pd_{79} (model **B,** Table S1) with adsorbate CH_3O in the transition state of C-O bond scission. Symmetry restrictions according to point group D_4.

	X	Y	Z
O	3.32998	3.31292	3.33813
O	-3.31292	3.32998	3.33813
O	3.31292	-3.32998	3.33813
O	-3.32998	-3.31292	3.33813
O	3.32998	-3.31292	-3.33813
O	-3.32998	3.31292	-3.33813
O	3.31292	3.32998	-3.33813
O	-3.31292	-3.32998	-3.33813
C	3.07322	5.18824	3.30527
C	-5.18824	3.07322	3.30527
C	5.18824	-3.07322	3.30527
C	-3.07322	-5.18824	3.30527
C	3.07322	-5.18824	-3.30527
C	-3.07322	5.18824	-3.30527
C	5.18824	3.07322	-3.30527
C	-5.18824	-3.07322	-3.30527
H	4.12713	5.29083	3.04964
H	-5.29083	4.12713	3.04964
H	5.29083	-4.12713	3.04964
H	-4.12713	-5.29083	3.04964
H	4.12713	-5.29083	-3.04964
H	-4.12713	5.29083	-3.04964
H	5.29083	4.12713	-3.04964
H	-5.29083	-4.12713	-3.04964
H	2.86134	5.11447	4.37061
H	-5.11447	2.86134	4.37061
H	5.11447	-2.86134	4.37061
H	-2.86134	-5.11447	4.37061
H	2.86134	-5.11447	-4.37061
H	-2.86134	5.11447	-4.37061
H	5.11447	2.86134	-4.37061
H	-5.11447	-2.86134	-4.37061
H	2.48076	6.02017	2.86052
H	-6.02017	2.48076	2.86052
H	6.02017	-2.48076	2.86052
H	-2.48076	-6.02017	2.86052
H	2.48076	-6.02017	-2.86052
H	-2.48076	6.02017	-2.86052
H	6.02017	2.48076	-2.86052
H	-6.02017	-2.48076	-2.86052

Table S5. Cartesian coordinates (Å) of all atoms of the cluster Pd_{79} (model **B,** Table S1) with CH_3 adsorbed at an on-top position on the (111) facets. Symmetry restrictions according to point group D_{4h}.

	X	Y	Z
C	3.13134	3.13134	5.08484
C	-3.13134	3.13134	5.08484
C	3.13134	-3.13134	5.08484
C	-3.13134	-3.13134	5.08484
C	3.13134	-3.13134	-5.08484
C	-3.13134	3.13134	-5.08484
C	3.13134	3.13134	-5.08484
C	-3.13134	-3.13134	-5.08484
H	2.47085	3.75875	5.69079
H	-3.75875	2.47085	5.69079
H	3.75875	-2.47085	5.69079
H	-2.47085	-3.75875	5.69079
H	2.47085	-3.75875	-5.69079
H	-2.47085	3.75875	-5.69079
H	3.75875	2.47085	-5.69079
H	-3.75875	-2.47085	-5.69079
H	-2.47085	-3.75875	-5.69079
H	3.75875	-2.47085	-5.69079
H	-3.75875	2.47085	-5.69079
H	2.47085	3.75875	-5.69079
H	-2.47085	3.75875	5.69079
H	2.47085	-3.75875	5.69079
H	-3.75875	-2.47085	5.69079
H	3.75875	2.47085	5.69079
H	3.73964	3.73964	4.40886
H	-3.73964	3.73964	4.40886
H	3.73964	-3.73964	4.40886
H	-3.73964	-3.73964	4.40886
H	3.73964	-3.73964	-4.40886
H	-3.73964	3.73964	-4.40886
H	3.73964	3.73964	-4.40886
H	-3.73964	-3.73964	-4.40886

Table S6. Cartesian coordinates (Å) of all atoms of the cluster Pd_{79} (model **B,** Table S1) with CH_3 adsorbed at bridge position on the (111) facets. Symmetry restrictions according to point group D_{4h}.

	X	Y	Z
C	3.98114	3.98114	3.00741
C	-3.98114	3.98114	3.00741
C	3.98114	-3.98114	3.00741
C	-3.98114	-3.98114	3.00741
C	3.98114	-3.98114	-3.00741
C	-3.98114	3.98114	-3.00741
C	3.98114	3.98114	-3.00741
C	-3.98114	-3.98114	-3.00741
H	3.34813	4.61704	3.64729
H	-4.61704	3.34813	3.64729
H	4.61704	-3.34813	3.64729
H	-3.34813	-4.61704	3.64729
H	3.34813	-4.61704	-3.64729
H	-3.34813	4.61704	-3.64729
H	4.61704	3.34813	-3.64729
H	-4.61704	-3.34813	-3.64729
H	-3.34813	-4.61704	-3.64729
H	4.61704	-3.34813	-3.64729
H	-4.61704	3.34813	-3.64729
H	3.34813	4.61704	-3.64729
H	-3.34813	4.61704	3.64729
H	3.34813	-4.61704	3.64729
H	-4.61704	-3.34813	3.64729
H	4.61704	3.34813	3.64729
H	4.61329	4.61329	2.37310
H	-4.61329	4.61329	2.37310
H	4.61329	-4.61329	2.37310
H	-4.61329	-4.61329	2.37310
H	4.61329	-4.61329	-2.37310
H	-4.61329	4.61329	-2.37310
H	4.61329	4.61329	-2.37310
H	-4.61329	-4.61329	-2.37310

Table S7. Cartesian coordinates (Å) of all atoms of the cluster Pd_{79} (model **B,** Table S1) with CH_3 adsorbed at a 3-fold fcc position on the (111) facets. Symmetry restrictions according to point group O_h.

	X	Y	Z
C	3.54140	3.54140	3.54140
C	3.54140	-3.54140	-3.54140
C	-3.54140	3.54140	-3.54140
C	-3.54140	-3.54140	3.54140
C	3.54140	-3.54140	3.54140
C	3.54140	3.54140	-3.54140
C	-3.54140	3.54140	3.54140
C	-3.54140	-3.54140	-3.54140
H	2.93081	4.18794	4.18794
H	2.93081	-4.18794	-4.18794
H	-2.93081	4.18794	-4.18794
H	-2.93081	-4.18794	4.18794
H	4.18794	2.93081	4.18794
H	-4.18794	2.93081	-4.18794
H	-4.18794	-2.93081	4.18794
H	4.18794	-2.93081	-4.18794
H	4.18794	4.18794	2.93081
H	4.18794	-4.18794	-2.93081
H	-4.18794	4.18794	-2.93081
H	-4.18794	-4.18794	2.93081
H	2.93081	-4.18794	4.18794
H	4.18794	4.18794	-2.93081
H	-4.18794	2.93081	4.18794
H	2.93081	4.18794	-4.18794
H	-4.18794	4.18794	2.93081
H	4.18794	-2.93081	4.18794
H	4.18794	2.93081	-4.18794
H	-4.18794	-2.93081	-4.18794
H	4.18794	-4.18794	2.93081
H	-2.93081	4.18794	4.18794
H	-4.18794	-4.18794	-2.93081
H	-2.93081	-4.18794	-4.18794

Table S8. Cartesian coordinates (Å) of all atoms of the cluster Pd_{79} with relaxed outer-most shell (model **R**). Symmetry restrictions according to point group O_h.

	X	Y	Z
Pd	0.00000	0.00000	0.00000
Pd	1.94454	1.94454	0.00000
Pd	1.94454	-1.94454	0.00000
Pd	-1.94454	1.94454	0.00000
Pd	-1.94454	-1.94454	0.00000
Pd	0.00000	1.94454	1.94454
Pd	0.00000	1.94454	-1.94454
Pd	0.00000	-1.94454	1.94454
Pd	0.00000	-1.94454	-1.94454
Pd	1.94454	0.00000	1.94454
Pd	1.94454	0.00000	-1.94454
Pd	-1.94454	0.00000	-1.94454
Pd	-1.94454	0.00000	1.94454
Pd	3.88909	0.00000	0.00000
Pd	-3.88909	0.00000	0.00000
Pd	0.00000	3.88909	0.00000
Pd	0.00000	-3.88909	0.00000
Pd	0.00000	0.00000	3.88909
Pd	0.00000	0.00000	-3.88909
Pd	3.94703	1.97351	1.97351
Pd	3.94703	-1.97351	-1.97351
Pd	-3.94703	1.97351	-1.97351
Pd	-3.94703	-1.97351	1.97351
Pd	1.97351	3.94703	1.97351
Pd	-1.97351	3.94703	-1.97351
Pd	-1.97351	-3.94703	1.97351
Pd	1.97351	-3.94703	-1.97351
Pd	1.97351	1.97351	3.94703
Pd	1.97351	-1.97351	-3.94703
Pd	-1.97351	1.97351	-3.94703
Pd	-1.97351	-1.97351	3.94703
Pd	3.94703	-1.97351	1.97351
Pd	1.97351	1.97351	-3.94703
Pd	-1.97351	3.94703	1.97351
Pd	3.94703	1.97351	-1.97351
Pd	-1.97351	1.97351	3.94703
Pd	1.97351	-3.94703	1.97351
Pd	1.97351	3.94703	-1.97351
Pd	-1.97351	-3.94703	-1.97351
Pd	1.97351	-1.97351	3.94703
Pd	-3.94703	1.97351	1.97351
Pd	-1.97351	-1.97351	-3.94703
Pd	-3.94703	-1.97351	-1.97351
Pd	3.88906	3.88906	0.00000
Pd	3.88906	-3.88906	0.00000
Pd	-3.88906	3.88906	0.00000
Pd	-3.88906	-3.88906	0.00000
Pd	0.00000	3.88906	3.88906
Pd	0.00000	3.88906	-3.88906
Pd	0.00000	-3.88906	3.88906
Pd	0.00000	-3.88906	-3.88906
Pd	3.88906	0.00000	3.88906

Pd	3.88906	0.00000	-3.88906
Pd	-3.88906	0.00000	-3.88906
Pd	-3.88906	0.00000	3.88906
Pd	5.81364	1.93788	0.00000
Pd	5.81364	-1.93788	0.00000
Pd	-5.81364	1.93788	0.00000
Pd	-5.81364	-1.93788	0.00000
Pd	0.00000	5.81364	1.93788
Pd	0.00000	5.81364	-1.93788
Pd	0.00000	-5.81364	1.93788
Pd	0.00000	-5.81364	-1.93788
Pd	1.93788	0.00000	5.81364
Pd	1.93788	0.00000	-5.81364
Pd	-1.93788	0.00000	-5.81364
Pd	-1.93788	0.00000	5.81364
Pd	5.81364	0.00000	1.93788
Pd	0.00000	1.93788	-5.81364
Pd	-1.93788	5.81364	0.00000
Pd	5.81364	0.00000	-1.93788
Pd	0.00000	1.93788	5.81364
Pd	1.93788	-5.81364	0.00000
Pd	1.93788	5.81364	0.00000
Pd	-1.93788	-5.81364	0.00000
Pd	0.00000	-1.93788	5.81364
Pd	-5.81364	0.00000	1.93788
Pd	0.00000	-1.93788	-5.81364
Pd	-5.81364	0.00000	-1.93788

Table S9. Cartesian coordinates (Å) of all atoms of the cluster Pd_{79} (model **R**) with adsorbed CH_3O. Symmetry restrictions according to point group O_h.

	X	Y	Z
Pd	0.00000	0.00000	0.00000
Pd	1.94454	1.94454	0.00000
Pd	1.94454	-1.94454	0.00000
Pd	-1.94454	1.94454	0.00000
Pd	-1.94454	-1.94454	0.00000
Pd	0.00000	1.94454	1.94454
Pd	0.00000	1.94454	-1.94454
Pd	0.00000	-1.94454	1.94454
Pd	0.00000	-1.94454	-1.94454
Pd	1.94454	0.00000	1.94454
Pd	1.94454	0.00000	-1.94454
Pd	-1.94454	0.00000	-1.94454
Pd	-1.94454	0.00000	1.94454
Pd	3.88909	0.00000	0.00000
Pd	-3.88909	0.00000	0.00000
Pd	0.00000	3.88909	0.00000
Pd	0.00000	-3.88909	0.00000
Pd	0.00000	0.00000	3.88909
Pd	0.00000	0.00000	-3.88909
Pd	3.94703	1.97351	1.97351
Pd	3.94703	-1.97351	-1.97351
Pd	-3.94703	1.97351	-1.97351
Pd	-3.94703	-1.97351	1.97351
Pd	1.97351	3.94703	1.97351
Pd	-1.97351	3.94703	-1.97351
Pd	-1.97351	-3.94703	1.97351
Pd	1.97351	-3.94703	-1.97351
Pd	1.97351	1.97351	3.94703
Pd	1.97351	-1.97351	-3.94703
Pd	-1.97351	1.97351	-3.94703
Pd	-1.97351	-1.97351	3.94703
Pd	3.94703	-1.97351	1.97351
Pd	1.97351	1.97351	-3.94703
Pd	-1.97351	3.94703	1.97351
Pd	3.94703	1.97351	-1.97351
Pd	-1.97351	1.97351	3.94703
Pd	1.97351	-3.94703	1.97351
Pd	1.97351	3.94703	-1.97351
Pd	-1.97351	-3.94703	-1.97351
Pd	1.97351	-1.97351	3.94703
Pd	-3.94703	1.97351	1.97351
Pd	-1.97351	-1.97351	-3.94703
Pd	-3.94703	-1.97351	-1.97351
Pd	3.88906	3.88906	0.00000
Pd	3.88906	-3.88906	0.00000
Pd	-3.88906	3.88906	0.00000
Pd	-3.88906	-3.88906	0.00000
Pd	0.00000	3.88906	3.88906
Pd	0.00000	3.88906	-3.88906
Pd	0.00000	-3.88906	3.88906
Pd	0.00000	-3.88906	-3.88906

Pd	3.88906	0.00000	3.88906
Pd	3.88906	0.00000	-3.88906
Pd	-3.88906	0.00000	-3.88906
Pd	-3.88906	0.00000	3.88906
Pd	5.81364	1.93788	0.00000
Pd	5.81364	-1.93788	0.00000
Pd	-5.81364	1.93788	0.00000
Pd	-5.81364	-1.93788	0.00000
Pd	0.00000	5.81364	1.93788
Pd	0.00000	5.81364	-1.93788
Pd	0.00000	-5.81364	1.93788
Pd	0.00000	-5.81364	-1.93788
Pd	1.93788	0.00000	5.81364
Pd	1.93788	0.00000	-5.81364
Pd	-1.93788	0.00000	-5.81364
Pd	-1.93788	0.00000	5.81364
Pd	5.81364	0.00000	1.93788
Pd	0.00000	1.93788	-5.81364
Pd	-1.93788	5.81364	0.00000
Pd	5.81364	0.00000	-1.93788
Pd	0.00000	1.93788	5.81364
Pd	1.93788	-5.81364	0.00000
Pd	1.93788	5.81364	0.00000
Pd	-1.93788	-5.81364	0.00000
Pd	0.00000	-1.93788	5.81364
Pd	-5.81364	0.00000	1.93788
Pd	0.00000	-1.93788	-5.81364
Pd	-5.81364	0.00000	-1.93788
O	3.51842	3.51842	3.51842
O	3.51842	-3.51842	-3.51842
O	-3.51842	3.51842	-3.51842
O	-3.51842	-3.51842	3.51842
O	3.51842	-3.51842	3.51842
O	3.51842	3.51842	-3.51842
O	-3.51842	3.51842	3.51842
O	-3.51842	-3.51842	-3.51842
C	4.34252	4.34252	4.34252
C	4.34252	-4.34252	-4.34252
C	-4.34252	4.34252	-4.34252
C	-4.34252	-4.34252	4.34252
C	4.34252	-4.34252	4.34252
C	4.34252	4.34252	-4.34252
C	-4.34252	4.34252	4.34252
C	-4.34252	-4.34252	-4.34252
H	3.71472	4.98148	4.98148
H	3.71472	-4.98148	-4.98148
H	-3.71472	4.98148	-4.98148
H	-3.71472	-4.98148	4.98148
H	4.98148	3.71472	4.98148
H	-4.98148	3.71472	-4.98148
H	-4.98148	-3.71472	4.98148
H	4.98148	-3.71472	-4.98148
H	4.98148	4.98148	3.71472
H	4.98148	-4.98148	-3.71472
H	-4.98148	4.98148	-3.71472
H	-4.98148	-4.98148	3.71472

H	3.71472	-4.98148	4.98148
H	4.98148	4.98148	-3.71472
H	-4.98148	3.71472	4.98148
H	3.71472	4.98148	-4.98148
H	-4.98148	4.98148	3.71472
H	4.98148	-3.71472	4.98148
H	4.98148	3.71472	-4.98148
H	-4.98148	-3.71472	-4.98148
H	4.98148	-4.98148	3.71472
H	-3.71472	4.98148	4.98148
H	-4.98148	-4.98148	-3.71472
H	-3.71472	-4.98148	-4.98148

Table S10. Cartesian coordinates (Å) of all atoms of the cluster Pd_{79} (model **R**) with the adsorbates O (fcc position on the (111) facet) and CH_3 (on-top, edge). Symmetry restrictions according to point group D_{4h}.

	X	Y	Z
Pd	0.00000	0.00000	0.00000
Pd	1.94454	1.94454	0.00000
Pd	-1.94454	1.94454	0.00000
Pd	1.94454	-1.94454	0.00000
Pd	-1.94454	-1.94454	0.00000
Pd	0.00000	1.94454	1.94454
Pd	-1.94454	0.00000	1.94454
Pd	1.94454	0.00000	1.94454
Pd	0.00000	-1.94454	1.94454
Pd	0.00000	-1.94454	-1.94454
Pd	0.00000	1.94454	-1.94454
Pd	1.94454	0.00000	-1.94454
Pd	-1.94454	0.00000	-1.94454
Pd	0.00000	0.00000	3.88909
Pd	0.00000	0.00000	-3.88909
Pd	3.88909	0.00000	0.00000
Pd	0.00000	3.88909	0.00000
Pd	0.00000	-3.88909	0.00000
Pd	-3.88909	0.00000	0.00000
Pd	3.98512	1.99256	1.99256
Pd	-1.99256	3.98512	1.99256
Pd	1.99256	-3.98512	1.99256
Pd	-3.98512	-1.99256	1.99256
Pd	3.98512	-1.99256	-1.99256
Pd	-3.98512	1.99256	-1.99256
Pd	1.99256	3.98512	-1.99256
Pd	-1.99256	-3.98512	-1.99256
Pd	-3.98512	-1.99256	-1.99256
Pd	1.99256	-3.98512	-1.99256
Pd	-1.99256	3.98512	-1.99256
Pd	3.98512	1.99256	-1.99256
Pd	-3.98512	1.99256	1.99256
Pd	3.98512	-1.99256	1.99256
Pd	-1.99256	-3.98512	1.99256
Pd	1.99256	3.98512	1.99256
Pd	1.98976	1.98976	3.97952
Pd	-1.98976	1.98976	3.97952
Pd	1.98976	-1.98976	3.97952
Pd	-1.98976	-1.98976	3.97952
Pd	1.98976	-1.98976	-3.97952
Pd	-1.98976	1.98976	-3.97952
Pd	1.98976	1.98976	-3.97952
Pd	-1.98976	-1.98976	-3.97952
Pd	3.90575	3.90575	0.00000
Pd	-3.90575	3.90575	0.00000
Pd	3.90575	-3.90575	0.00000
Pd	-3.90575	-3.90575	0.00000
Pd	0.00000	3.93541	3.93541
Pd	-3.93541	0.00000	3.93541
Pd	3.93541	0.00000	3.93541

Pd	0.00000	-3.93541	3.93541
Pd	0.00000	-3.93541	-3.93541
Pd	0.00000	3.93541	-3.93541
Pd	3.93541	0.00000	-3.93541
Pd	-3.93541	0.00000	-3.93541
Pd	5.80952	1.93651	0.00000
Pd	-1.93651	5.80952	0.00000
Pd	1.93651	-5.80952	0.00000
Pd	-5.80952	-1.93651	0.00000
Pd	5.80952	-1.93651	0.00000
Pd	-5.80952	1.93651	0.00000
Pd	1.93651	5.80952	0.00000
Pd	-1.93651	-5.80952	0.00000
Pd	5.82606	0.00000	1.94202
Pd	0.00000	5.82606	1.94202
Pd	0.00000	-5.82606	1.94202
Pd	-5.82606	0.00000	1.94202
Pd	5.82606	0.00000	-1.94202
Pd	-5.82606	0.00000	-1.94202
Pd	0.00000	5.82606	-1.94202
Pd	0.00000	-5.82606	-1.94202
Pd	0.00000	1.94094	5.82281
Pd	-1.94094	0.00000	5.82281
Pd	1.94094	0.00000	5.82281
Pd	0.00000	-1.94094	5.82281
Pd	0.00000	-1.94094	-5.82281
Pd	0.00000	1.94094	-5.82281
Pd	1.94094	0.00000	-5.82281
Pd	-1.94094	0.00000	-5.82281
C	0.00000	5.36693	5.36693
C	-5.36693	0.00000	5.36693
C	5.36693	0.00000	5.36693
C	0.00000	-5.36693	5.36693
C	0.00000	-5.36693	-5.36693
C	0.00000	5.36693	-5.36693
C	5.36693	0.00000	-5.36693
C	-5.36693	0.00000	-5.36693
H	0.00000	6.33455	4.84383
H	-6.33455	0.00000	4.84383
H	6.33455	0.00000	4.84383
H	0.00000	-6.33455	4.84383
H	0.00000	-6.33455	-4.84383
H	0.00000	6.33455	-4.84383
H	6.33455	0.00000	-4.84383
H	-6.33455	0.00000	-4.84383
H	0.91163	5.24678	5.96411
H	-5.24678	0.91163	5.96411
H	5.24678	-0.91163	5.96411
H	-0.91163	-5.24678	5.96411
H	0.91163	-5.24678	-5.96411
H	-0.91163	5.24678	-5.96411
H	5.24678	0.91163	-5.96411
H	-5.24678	-0.91163	-5.96411
H	-0.91163	-5.24678	-5.96411
H	5.24678	-0.91163	-5.96411
H	-5.24678	0.91163	-5.96411

H	0.91163	5.24678	-5.96411
H	-0.91163	5.24678	5.96411
H	0.91163	-5.24678	5.96411
H	-5.24678	-0.91163	5.96411
H	5.24678	0.91163	5.96411
O	3.30510	3.30510	3.30510
O	-3.30510	3.30510	3.30510
O	3.30510	-3.30510	3.30510
O	-3.30510	-3.30510	3.30510
O	3.30510	-3.30510	-3.30510
O	-3.30510	3.30510	-3.30510
O	3.30510	3.30510	-3.30510
O	-3.30510	-3.30510	-3.30510

Table S11. Cartesian coordinates (Å) of all atoms of the cluster Pd_{79} (model **R**) with CH_3 adsorbed at an on-top position on the (111) facets. Symmetry restrictions according to point group D_{4h}.

	X	Y	Z
Pd	0.00000	0.00000	0.00000
Pd	1.94454	1.94454	0.00000
Pd	-1.94454	1.94454	0.00000
Pd	1.94454	-1.94454	0.00000
Pd	-1.94454	-1.94454	0.00000
Pd	0.00000	1.94454	1.94454
Pd	-1.94454	0.00000	1.94454
Pd	1.94454	0.00000	1.94454
Pd	0.00000	-1.94454	1.94454
Pd	0.00000	-1.94454	-1.94454
Pd	0.00000	1.94454	-1.94454
Pd	1.94454	0.00000	-1.94454
Pd	-1.94454	0.00000	-1.94454
Pd	0.00000	0.00000	3.88909
Pd	0.00000	0.00000	-3.88909
Pd	3.88909	0.00000	0.00000
Pd	0.00000	3.88909	0.00000
Pd	0.00000	-3.88909	0.00000
Pd	-3.88909	0.00000	0.00000
Pd	3.91746	1.95873	1.95873
Pd	-1.95873	3.91746	1.95873
Pd	1.95873	-3.91746	1.95873
Pd	-3.91746	-1.95873	1.95873
Pd	3.91746	-1.95873	-1.95873
Pd	-3.91746	1.95873	-1.95873
Pd	1.95873	3.91746	-1.95873
Pd	-1.95873	-3.91746	-1.95873
Pd	-3.91746	-1.95873	-1.95873
Pd	1.95873	-3.91746	-1.95873
Pd	-1.95873	3.91746	-1.95873
Pd	3.91746	1.95873	-1.95873
Pd	-3.91746	1.95873	1.95873
Pd	3.91746	-1.95873	1.95873
Pd	-1.95873	-3.91746	1.95873
Pd	1.95873	3.91746	1.95873
Pd	1.97815	1.97815	3.95630
Pd	-1.97815	1.97815	3.95630
Pd	1.97815	-1.97815	3.95630
Pd	-1.97815	-1.97815	3.95630
Pd	1.97815	-1.97815	-3.95630
Pd	-1.97815	1.97815	-3.95630
Pd	1.97815	1.97815	-3.95630
Pd	-1.97815	-1.97815	-3.95630
Pd	3.88315	3.88315	0.00000
Pd	-3.88315	3.88315	0.00000
Pd	3.88315	-3.88315	0.00000
Pd	-3.88315	-3.88315	0.00000
Pd	0.00000	3.89705	3.89705
Pd	-3.89705	0.00000	3.89705
Pd	3.89705	0.00000	3.89705

Pd	0.00000	-3.89705	3.89705
Pd	0.00000	-3.89705	-3.89705
Pd	0.00000	3.89705	-3.89705
Pd	3.89705	0.00000	-3.89705
Pd	-3.89705	0.00000	-3.89705
Pd	5.79849	1.93283	0.00000
Pd	-1.93283	5.79849	0.00000
Pd	1.93283	-5.79849	0.00000
Pd	-5.79849	-1.93283	0.00000
Pd	5.79849	-1.93283	0.00000
Pd	-5.79849	1.93283	0.00000
Pd	1.93283	5.79849	0.00000
Pd	-1.93283	-5.79849	0.00000
Pd	5.79588	0.00000	1.93196
Pd	0.00000	5.79588	1.93196
Pd	0.00000	-5.79588	1.93196
Pd	-5.79588	0.00000	1.93196
Pd	5.79588	0.00000	-1.93196
Pd	-5.79588	0.00000	-1.93196
Pd	0.00000	5.79588	-1.93196
Pd	0.00000	-5.79588	-1.93196
Pd	0.00000	1.93771	5.81313
Pd	-1.93771	0.00000	5.81313
Pd	1.93771	0.00000	5.81313
Pd	0.00000	-1.93771	5.81313
Pd	0.00000	-1.93771	-5.81313
Pd	0.00000	1.93771	-5.81313
Pd	1.93771	0.00000	-5.81313
Pd	-1.93771	0.00000	-5.81313
C	3.16516	3.16516	5.13977
C	-3.16516	3.16516	5.13977
C	3.16516	-3.16516	5.13977
C	-3.16516	-3.16516	5.13977
C	3.16516	-3.16516	-5.13977
C	-3.16516	3.16516	-5.13977
C	3.16516	3.16516	-5.13977
C	-3.16516	-3.16516	-5.13977
H	2.50346	3.79230	5.74497
H	-3.79230	2.50346	5.74497
H	3.79230	-2.50346	5.74497
H	-2.50346	-3.79230	5.74497
H	2.50346	-3.79230	-5.74497
H	-2.50346	3.79230	-5.74497
H	3.79230	2.50346	-5.74497
H	-3.79230	-2.50346	-5.74497
H	-2.50346	-3.79230	-5.74497
H	3.79230	-2.50346	-5.74497
H	-3.79230	2.50346	-5.74497
H	2.50346	3.79230	-5.74497
H	-2.50346	3.79230	5.74497
H	2.50346	-3.79230	5.74497
H	-3.79230	-2.50346	5.74497
H	3.79230	2.50346	5.74497
H	3.77311	3.77311	4.46274
H	-3.77311	3.77311	4.46274
H	3.77311	-3.77311	4.46274

H	-3.77311	-3.77311	4.46274
H	3.77311	-3.77311	-4.46274
H	-3.77311	3.77311	-4.46274
H	3.77311	3.77311	-4.46274
H	-3.77311	-3.77311	-4.46274

Table S11. Cartesian coordinates (Å) of all atoms of the cluster Pd_{79} (model **R**) with CH_3 adsorbed at an on-top position of cluster edge. Symmetry restrictions according to point group D_{4h}.

	X	Y	Z
Pd	0.00000	0.00000	0.00000
Pd	1.94454	1.94454	0.00000
Pd	-1.94454	1.94454	0.00000
Pd	1.94454	-1.94454	0.00000
Pd	-1.94454	-1.94454	0.00000
Pd	0.00000	1.94454	1.94454
Pd	-1.94454	0.00000	1.94454
Pd	1.94454	0.00000	1.94454
Pd	0.00000	-1.94454	1.94454
Pd	0.00000	-1.94454	-1.94454
Pd	0.00000	1.94454	-1.94454
Pd	1.94454	0.00000	-1.94454
Pd	-1.94454	0.00000	-1.94454
Pd	0.00000	0.00000	3.88909
Pd	0.00000	0.00000	-3.88909
Pd	3.88909	0.00000	0.00000
Pd	0.00000	3.88909	0.00000
Pd	0.00000	-3.88909	0.00000
Pd	-3.88909	0.00000	0.00000
Pd	3.91597	1.95798	1.95798
Pd	-1.95798	3.91597	1.95798
Pd	1.95798	-3.91597	1.95798
Pd	-3.91597	-1.95798	1.95798
Pd	3.91597	-1.95798	-1.95798
Pd	-3.91597	1.95798	-1.95798
Pd	1.95798	3.91597	-1.95798
Pd	-1.95798	-3.91597	-1.95798
Pd	-3.91597	-1.95798	-1.95798
Pd	1.95798	-3.91597	-1.95798
Pd	-1.95798	3.91597	-1.95798
Pd	3.91597	1.95798	-1.95798
Pd	-3.91597	1.95798	1.95798
Pd	3.91597	-1.95798	1.95798
Pd	-1.95798	-3.91597	1.95798
Pd	1.95798	3.91597	1.95798
Pd	1.95629	1.95629	3.91259
Pd	-1.95629	1.95629	3.91259
Pd	1.95629	-1.95629	3.91259
Pd	-1.95629	-1.95629	3.91259
Pd	1.95629	-1.95629	-3.91259
Pd	-1.95629	1.95629	-3.91259
Pd	1.95629	1.95629	-3.91259
Pd	-1.95629	-1.95629	-3.91259
Pd	3.88569	3.88569	0.00000
Pd	-3.88569	3.88569	0.00000
Pd	3.88569	-3.88569	0.00000
Pd	-3.88569	-3.88569	0.00000
Pd	0.00000	3.91495	3.91495
Pd	-3.91495	0.00000	3.91495
Pd	3.91495	0.00000	3.91495

Pd	0.00000	-3.91495	3.91495
Pd	0.00000	-3.91495	-3.91495
Pd	0.00000	3.91495	-3.91495
Pd	3.91495	0.00000	-3.91495
Pd	-3.91495	0.00000	-3.91495
Pd	5.79184	1.93061	0.00000
Pd	-1.93061	5.79184	0.00000
Pd	1.93061	-5.79184	0.00000
Pd	-5.79184	-1.93061	0.00000
Pd	5.79184	-1.93061	0.00000
Pd	-5.79184	1.93061	0.00000
Pd	1.93061	5.79184	0.00000
Pd	-1.93061	-5.79184	0.00000
Pd	5.80960	0.00000	1.93653
Pd	0.00000	5.80960	1.93653
Pd	0.00000	-5.80960	1.93653
Pd	-5.80960	0.00000	1.93653
Pd	5.80960	0.00000	-1.93653
Pd	-5.80960	0.00000	-1.93653
Pd	0.00000	5.80960	-1.93653
Pd	0.00000	-5.80960	-1.93653
Pd	0.00000	1.93354	5.80062
Pd	-1.93354	0.00000	5.80062
Pd	1.93354	0.00000	5.80062
Pd	0.00000	-1.93354	5.80062
Pd	0.00000	-1.93354	-5.80062
Pd	0.00000	1.93354	-5.80062
Pd	1.93354	0.00000	-5.80062
Pd	-1.93354	0.00000	-5.80062
C	0.00000	5.34844	5.34844
C	-5.34844	0.00000	5.34844
C	5.34844	0.00000	5.34844
C	0.00000	-5.34844	5.34844
C	0.00000	-5.34844	-5.34844
C	0.00000	5.34844	-5.34844
C	5.34844	0.00000	-5.34844
C	-5.34844	0.00000	-5.34844
H	0.00000	6.31994	4.83468
H	-6.31994	0.00000	4.83468
H	6.31994	0.00000	4.83468
H	0.00000	-6.31994	4.83468
H	0.00000	-6.31994	-4.83468
H	0.00000	6.31994	-4.83468
H	6.31994	0.00000	-4.83468
H	-6.31994	0.00000	-4.83468
H	0.90944	5.22262	5.94791
H	-5.22262	0.90944	5.94791
H	5.22262	-0.90944	5.94791
H	-0.90944	-5.22262	5.94791
H	0.90944	-5.22262	-5.94791
H	-0.90944	5.22262	-5.94791
H	5.22262	0.90944	-5.94791
H	-5.22262	-0.90944	-5.94791
H	-0.90944	-5.22262	-5.94791
H	5.22262	-0.90944	-5.94791
H	-5.22262	0.90944	-5.94791

H	0.90944	5.22262	-5.94791
H	-0.90944	5.22262	5.94791
H	0.90944	-5.22262	5.94791
H	-5.22262	-0.90944	5.94791
H	5.22262	0.90944	5.94791