Table S1. Binding energy, geometry and charge transfer to O* on closed-packed 4x4 platinum group and coinage metal surfaces.

	BE^{rad}	BE^{mol}	M—M stretch[a]	O z-dist[b]	O—M[c]	O*[d]	M$_1$[e]	M$_{2+}$[f]	Site
	eV	eV	%	Å	Å				
Ru(0001)	-5.70	-2.81	5.84	1.24	2.02	-0.58	+0.51	+0.06	3fh
Rh(111)	-4.85	-1.96	0.93	1.36	2.02	-0.56	+0.53	+0.03	3ff
Pd(111)	-4.08	-1.19	4.04	1.21	2.01	-0.55	+0.73	-0.18	3ff
Os(0001)	-5.51	-2.62	6.11	1.27	2.06	-0.64	+0.42	+0.22	3fh
Ir(111)	-4.54	-1.65	1.71	1.39	2.06	-0.64	+0.43	+0.22	3ff
Pt(111)	-3.91	-1.01	5.76	1.22	2.06	-0.61	+0.60	+0.00	3ff
Cu(111)	-4.46	-1.57	4.58	1.24	1.92	-1.06	+1.02	+0.04	3ff
Ag(111)	-3.17	-0.28	4.74	1.36	2.18	-1.04	+0.82	+0.22	3ff
Au(111)	-2.68	+0.21	9.74	1.22	2.16	-0.96	+0.63	+0.32	3ff

[a]The percent-increase of the three M-M bonds comprising the three-fold site over the bulk M-M bond distance. [b]The distance of the O* atom perpendicular to the surface plane [c]The average O—M bond distance for the three O-M bonds in the 3-fold site. [d]The charge on the O* adsorbate. [e]The total charge on the metal atoms which the O* adsorbate is bound directly to (the ensemble metal atoms). [f]The total charge on all other metals in the system (non-ensemble).
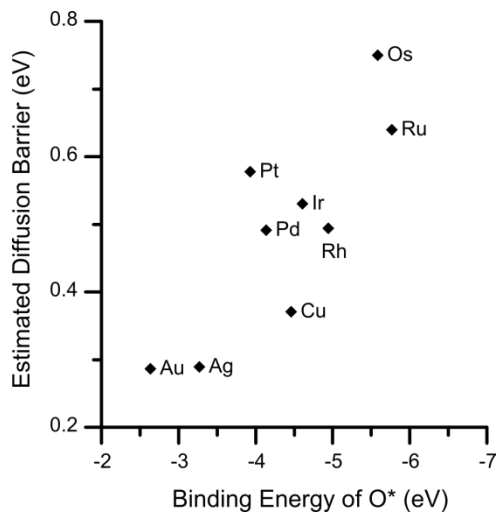

Figure S1. Correlation between the estimated diffusion barrier and binding energy of O* on various transition metal surfaces.

Table S2. Charge Distribution of O* Bound on a 4x4 Closed-Packed Metal Surface of Various Metals in Various Binding Modes

$O^{*\,a}$ $M_1{}^b$ $M_{2+}{}^c$	atop	bridge	3fh	3ff
Ru(0001)	-0.44	-0.59	-0.58	-0.60
	+0.35	+0.22	+0.51	+0.49
	-0.10	-0.37	-0.06	-0.11
Rh(111)	-0.51	-0.56	-0.55	-0.55
	+0.37	+0.23	+0.51	+0.53
	-0.14	-0.33	-0.04	-0.03
Pd(111)	-0.54	-0.56	-0.54	-0.55
	+0.38	+0.33	+0.71	+0.73
	-0.16	-0.23	+0.17	+0.18
Os(0001)	-0.45	-0.65	-0.64	-0.66
	+0.36	+0.18	+0.41	+0.42
	-0.09	-0.47	-0.22	-0.24
Ir(111)	-0.50	-0.63	-0.63	-0.64
	+0.41	+0.20	+0.42	+0.43
	-0.07	-0.43	-0.21	-0.21
Pt(111)	-0.54	-0.60	-0.59	-0.61
	+0.45	+0.27	+0.60	+0.60
	-0.09	-0.34	+0.01	0.00
Cu(111)	-0.96	-1.05	-1.05	-1.06
	+0.32	+0.51	+0.92	+1.02
	-0.64	-0.54	-0.13	-0.04
Ag(111)	-0.92	-1.02	-1.01	-1.03
	+0.30	+0.46	+0.78	+0.82
	-0.63	-0.56	-0.25	-0.22
Au(111)	-0.80	-0.92	-0.92	-0.96
	+0.40	+0.35	+0.66	+0.63
	-0.41	-0.57	-0.26	-0.32

[a]Charge on the O* adsorbate. [b]Total charge on the metal atoms which the O* adsorbate is bound directly to (the ensemble metal atoms). [c]Total charge on all other metals in the system.

If we examine the charges on the metal atoms which bind directly to the O* (referred to as *ensemble* metals), we can see that in the atop position, the metal atom has a charge between 0.32 and 0.49, and as you increase the coordination of the O* with the metal, the charge on each metal atom of the ensemble decreases, but the increase in coordination results in greater total charge from the ensemble metals. The charge on the rest of the metal atoms follows the opposite trend, with O* in atop and bridge sites withdrawing significant amounts of charge from non-ensemble metals while in 3ff and 3fh withdrawing very little from non-ensemble atoms. Ultimately, when O* is placed on a metal surface it will withdraw 0.5 to 0.8 e^- from a non-coinage metal and ~1 e^- from a coinage metal. A comparison of the binding modes reveal that as O* shifts from highly stable 3ff and 3fh sites to less-coordinated bridge and atop sites, it maintains most of its negative charge, withdrawing more electrons from its ensemble metals and making up for the rest by depleting charge from vicinal non-ensemble metals through the M-M interactions with the ensemble metals.
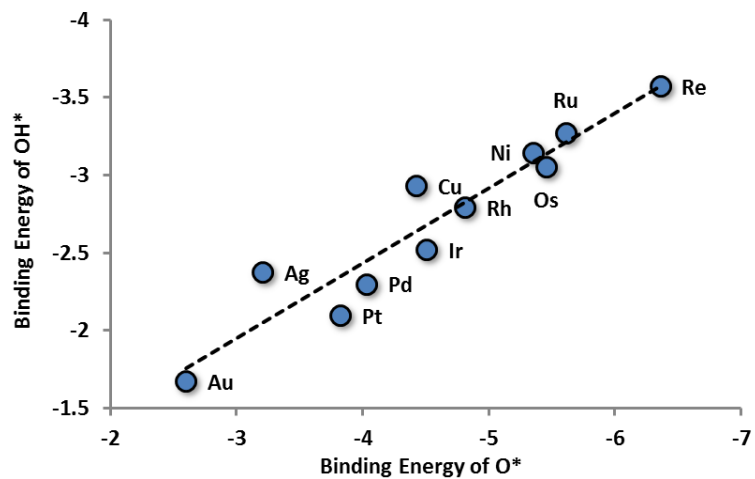
Figure S2. Correlation between the BE^{rad} of O* and OH* on closed-packed metal surfaces.

Table S3. Charge Distribution of OH* Bound on Various Transition Metals and Binding Modes

H* O* $M_1{}^a$ $M_{2+}{}^b$	atop	bridge	3fh	3ff
Ru(0001)	0.40	0.41	0.44	0.44
	-0.74	-0.73	-0.74	-0.76
	0.2	0.25	0.26	0.29
	0.13	0.07	0.03	0.02
Rh(111)	0.40	0.41	0.44	0.44
	-0.73	-0.73	-0.77	-0.76
	0.22	0.28	0.32	0.32
	0.11	0.04	0.01	0.00
Pd(111)	0.40	0.41	0.44	0.44
	-0.75	-0.75	-0.81	-0.80
	0.29	0.39	0.45	0.48
	0.07	-0.05	-0.08	-0.12
Os(0001)	0.40	0.41	0.46	0.45
	-0.76	-0.77	-0.80	-0.82
	0.19	0.21	0.18	0.20
	0.17	0.16	0.16	0.16
Ir(111)	0.40	0.41	0.45	0.46
	-0.76	-0.75	-0.83	-0.82
	0.24	0.26	0.27	0.25
	0.12	0.08	0.11	0.11
Pt(111)	0.41	0.41	0.45	0.46
	-0.77	-0.76	-0.87	-0.85
	0.31	0.37	0.37	0.40
	0.05	-0.02	0.05	0.00
Cu(111)	0.40	0.42	0.44	0.44
	-0.99	-1.02	-1.05	-1.05
	0.31	0.55	0.64	0.62
	0.29	0.05	-0.03	-0.02
Ag(111)	0.40	0.41	0.43	0.43
	-1.01	-1.04	-1.07	-1.07
	0.28	0.47	0.57	0.57
	0.33	0.16	0.07	0.07
Au(111)	0.40	0.40	0.44	0.44
	-0.93	-0.96	-1.04	-1.04
	0.30	0.38	0.43	0.44
	0.23	0.17	0.18	0.17

[a]The total charge on the metal atoms which the OH* adsorbate is bound directly to. [b]The total charge on all other metals in the system.

The O-atom on OH* withdraws 0.4-0.46 e^- from the hydrogen atom, as such, the metal is less positively charged than in the case of O* adsorption. For OH* bound atop of the metal, the ligand metal takes on a 0.2-0.3 charge with non-ligand metals contributing 0.04-0.17 e^- for non-coinage metals and 0.26-0.34 e^- for the coinage metals. For OH* at the bridge and 3-fold sites, the total charge on the ligand metals increases while the charge on each metal ligand atom decreases and the non-ligand atoms are slightly negative or slightly positive in charge.
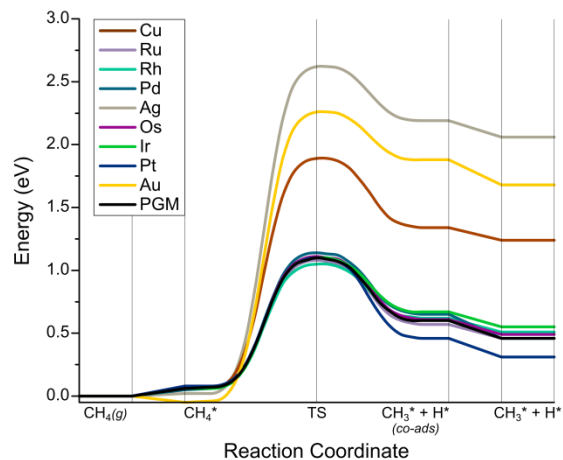
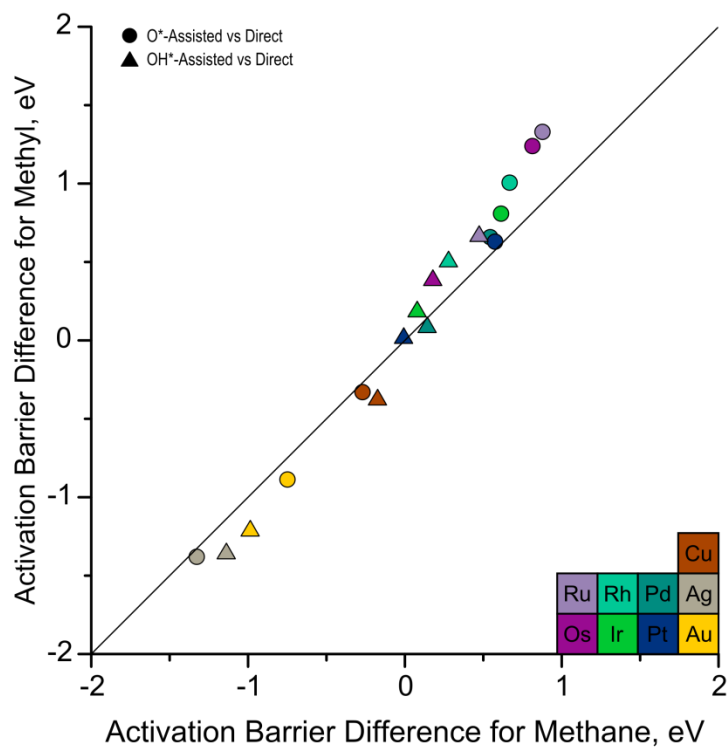**Figure S3.** Reaction energetics for methane dissociation on closed-packed transition metal surfaces.

Figure S4. A comparison of the effect of O*- and OH*-assistance on the C-H activation barriers of methyl and methane.
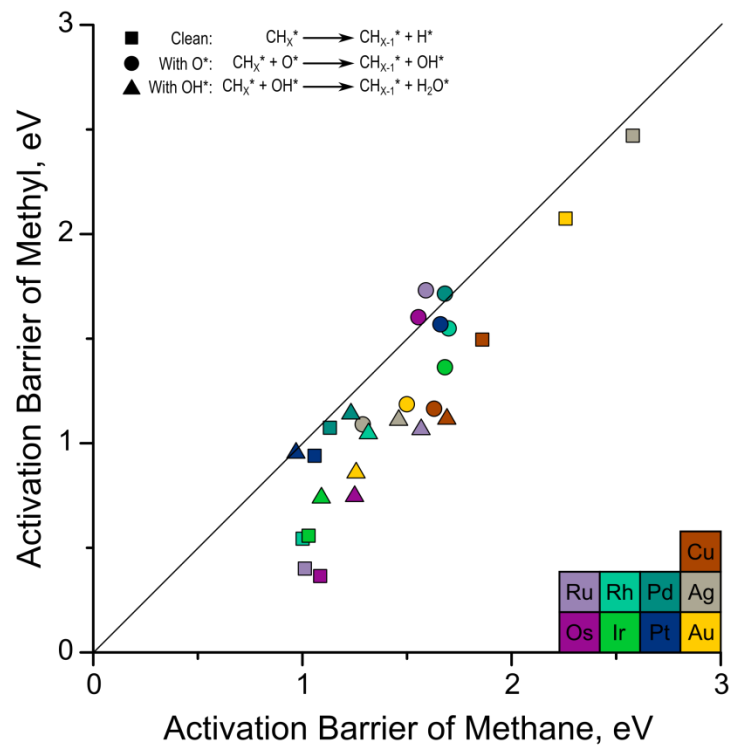
Figure S5. A comparison of the C-H activation barriers of methane and methyl through direct, O*-assisted and OH*-assisted reactions on platinum-group and coinage metals.