Electronic Supplementary Information (ESI)

Interaction of Ethene and Ethyne with Bare and Hydrogenated Ir₄ Clusters. A Density Functional Study

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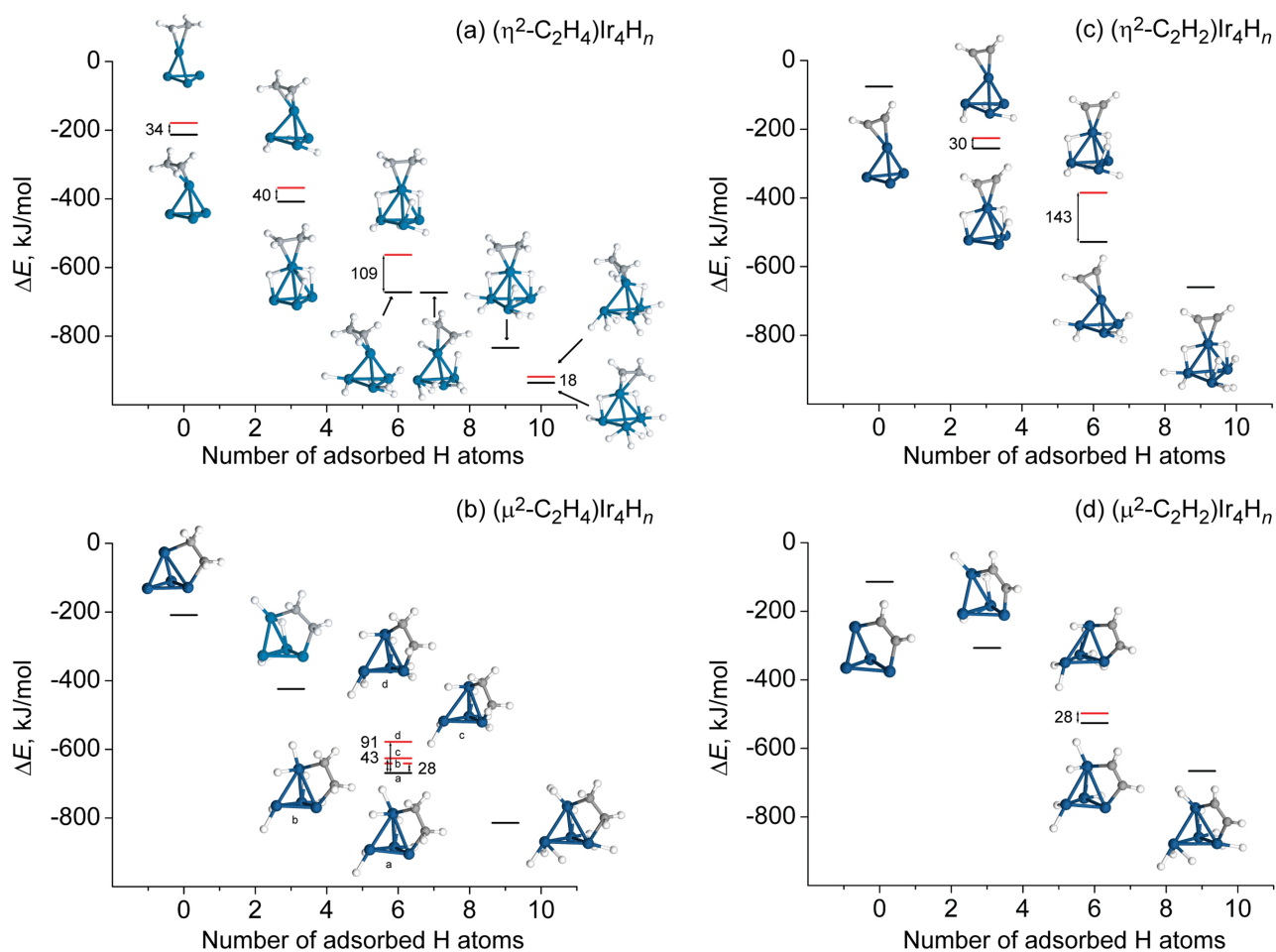## S1. Ethene / ethyne adsorption on hydrogenated iridium clusters

Figure S1. Relative stability of different optimized isomers of the complexes obtained by adsorption of ethene and ethyne to bare and hydrogenated Ir_4 clusters: (a) π-coordinated ethene; (b) di-σ-coordinated ethene; (c) π-coordinated ethyne; (d) di-σ-coordinated ethyne.

In the series of complexes with di-σ-coordinated ethene, (di-σ -C_2H_4)Ir_4H_n, different isomers were considered only for the structure with 6 H ligands. The complexes **a** and **b**, on the one hand, and **c** and **d**, on the other, have similar structures but different spin state (see Fig. S1b). The most stable among them is the complex denoted as **a** in which two of the hydrogen ligands are coordinated in on-top mode to one of the iridium atoms connected with the organic ligand while no hydrogen ligand is coordinated to the other iridium center participating in the coordination of the organic molecule. Coordination of a hydrogen atom to each of the iridium atoms involved in the coordination of the organic ligand results in destabilization of the structure by more than 40 kJ/mol.

Table S1. Coefficients of the linear functions $\Delta G = A + B \times k$ ($k = n + m$) showing the dependence of the relative Gibbs free energy of the model complexes $(C_2H_m)Ir_4H_n$ ($m = 2$–5; $n = 0, 3, 6, 9$) on the total number of H atoms in the system, k. R^2 is the correlation coefficient obtained at the regression analysis of the linear functions.

Series	A [kJ/mol]	B [kJ/mol per H]	R^2
π-$H_2CH_2CIr_4H_n$	98.47	-67.65	0.995
di-σ-$H_2CH_2CIr_4H_n$	74.21	-64.36	0.986
π-$HCHCIr_4H_n$	98.17	-63.90	0.986
di-σ-$HCHCIr_4H_n$	34.98	-58.03	0.988
$H_3CH_2CIr_4H_n$	108.21	-63.16	0.965
$H_3CCIr_4H_n$			
$\quad k \leq 6$	252.36	-111.17	0.999
$\quad k \geq 6$	210.36	-34.06	0.966
$H_2CHCIr_4H_n$	207.86	-68.27	0.978
$H_2CCIr_4H_n$	139.42	-64.73	0.965

Determination of the concentrations of the various species formed after H_2 and C_2H_4 adsorption on an Ir_4 cluster

We provide pertinent information for constructing the thermodynamic model of hydrogen and ethene adsorption on Ir_4H_n clusters in the gas phase. Initially the system is considered to comprise a bare Ir_4 cluster, H_2, and C_2H_4. Mainly two main types of adsorption complexes can be formed: Ir_4H_n species without an organic ligand and $C_2H_mIr_4H_n$ species with an organic ligand of various kinds and coordination modes:

$$Ir_4 + \frac{n+m-4}{2}H_2 + C_2H_4 \rightarrow C_2H_mIr_4H_n \tag{1}$$

$$Ir_4 + \frac{n}{2}H_2 \rightarrow Ir_4H_n \tag{2}$$
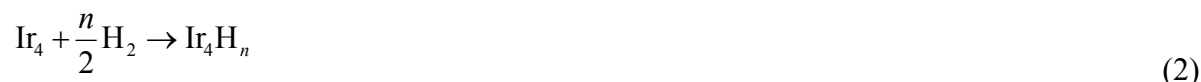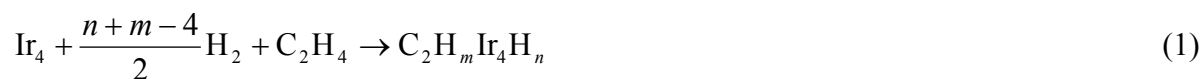
The Gibbs free energy of formation of the hydrogenated Ir_4H_n species and the adsorption complexes with an organic ligand can be calculated with respect to Eqs. (1) and (2) as follows:

$$\begin{aligned}
\Delta G[n{:}m] &= \left[E[n{:}m] - E[0:0] - E[C_2H_4] - yE[H_2]\right] + \\
&\quad + \left[ZPE[n:m] - ZPE[0:0] - ZPE[C_2H_4] - yZPE[H_2]\right] - \\
&\quad - T \times \left[S[n:m] - S[0:0] - S[C_2H_4] - yS[H_2]\right] \\
&= \Delta E[n:m] + \Delta ZPE[n:m] - T \times \Delta S[n:m]
\end{aligned} \tag{3}$$

$$\Delta G[n{:}0] = \Delta E[n:0] + \Delta ZPE[n:0] - T \times \Delta S[n:0] \tag{4}$$

The concentrations of the various complexes can be obtained via Eqs. (5) and (6), taking into account that the sum of the concentrations of all Ir_4-containing species is normalized to one:

$$[n{:}m] = [0:0] \times K[n:m] \times \left(\frac{P(H_2)}{RT}\right)^y \times \left(\frac{P(C_2H_4)}{RT}\right) \tag{5}$$

$$[n{:}0] = [0:0] \times K[n:0] \times \left(\frac{P(H_2)}{RT}\right)^{\frac{n}{2}} \tag{6}$$

$$\sum_{n=0}^{14-m}\sum_{m=2}^{5}[n:m] + \sum_{n=0}^{10}[n:0] = 1 \tag{7}$$

$$[0{:}0] = \left\{\sum_{n=0}^{14-m}\sum_{m=2}^{5}K[n:m] \times \left(\frac{P(H_2)}{RT}\right)^y \times \left(\frac{P(C_2H_4)}{RT}\right) + \sum_{n=0}^{10}K[n:0] \times \left(\frac{P(H_2)}{RT}\right)^{\frac{n}{2}}\right\}^{-1} \tag{8}$$

In the above equations, we used the following notations:

$$y = \frac{n+m-4}{2}$$

[n:m] – concentration of $C_2H_mIr_4H_n$
[n:0] – concentration of Ir_4H_n
[0:0] – concentration of Ir_4
$K[n:m] = \exp\{-\Delta G[n:m]/RT\}$

Experimental data from IR spectroscopy investigation of ethene / ethyne adsorption on metal surfaces and supported metal clusters

Table S2. Experimental vibrational frequencies of ethene or ethene-derived species adsorbed on supported iridium species or iridium surface.

Catalysts	IR bands, cm^{-1}	Adsorbate	Conditions	Ref.
Ir$_4$/γ-Al$_2$O$_3$	2988, 2975, 2897, 2884 2956, 2933	di-σ-bonded ethene ethyl	288 K 300 Torr H$_2$ 40-200 Torr C$_2$H$_4$	1
	2992, 2987, 2896, 2887 2957, 2929, 2863 3060, 3026 2947, 2896	di-σ-bonded ethene ethyl π-bonded ethene ethylidyne	288 K 300 Torr H$_2$ 200-293 Torr C$_2$H$_4$	
Ir$_n$/γ-Al$_2$O$_3$ ^{a}	1480, 1186 2887 [$v_s(CH_3)$], 1346 [$\delta_s(CH_3)$]	ethene ethylidyne	90 K 300 K	2
Ir/Al$_2$O$_3$ ^{b}	2947, 2896, 2816, 1418, 1350, 1156 2978, 1504, 1188	ethylidyne π-bonded ethene	room temperature	3
Ir(111) ^{c}	2940 [$v_s(CH_3)$], 1400 [$\delta_s(CH_3)$], 1165 [$v(CC)$], 986 [$\rho(CH_3)$], 457 [$v_s(CM)$]	ethylidyne	180 K 4×10^{-4} Pa s C$_2$H$_4$	4
	2950 [$v_s(CH_3)$], 1410 [$\delta_s(CH_3)$], 1600 [$v(CC)$], 986 [$\rho(CH_3)$], 780 [$\delta(CH)$], ~430 [$v_s(CM)$]	ethylidyne	180 K 5×10^{-4} Pa s C$_2$H$_2$	
	3020, 1280, 830	acetylide (CCH) / polymers	300→450 K 10×10^{-4} Pa s C$_2$H$_2$	
Ir(210) ^{b}	2949, 1441, 791	acetylide (CCH)	90 K 0.5 langmuir C$_2$H$_2$	5
	2970, 1448, 1136, 988	ethylidyne	90 K 3 langmuir C$_2$H$_2$	

^{a} Particles of ca. 350 Ir atoms. ^{b} Particle size estimated 1.8 nm (100–150 atoms) by CO titration. ^{c} HREELS.

(1) Argo, A. M.; Odzak, J. F.; Gates, B. C. *J. Am. Chem. Soc.* **2003**, *125*, 7107–7115.
(2) Frank, M.; Bäumer, M.; Kuhnemuth, R.; Freund H.-J. *J. Vac. Sci. Tech. A* **2001**, *19*, 1497–1501.
(3) Mohsin, S. B.; Trenary, M.; Robota, H. J. *J. Phys. Chem.* **1991**, *95*, 6657–6661.
(4) Marinova, Ts. S.; Kostov, K. L. *Surf. Sci.* **1987**, *181*, 573–585.
(5) Chen, W.; Ermanoski, I.; Wu, Q.; Madey, T. E.; Hwu, H. H.; Chen, J. G. *J. Phys. Chem. B* **2003**, *107*, 5231–5242.

Table S3. Comparison between the experimental and theoretical spectra of ethene and ethyne in gas phase and adsorbed on iridium clusters in π- or di-σ-mode. The theoretically obtained values have not been corrected; the experimental values for the adsorbed species are from Ref. 1.

Structure	ν(C-H)	δ(C-H)	ν(C-C)
Experimental values			
C_2H_6	2896, 2954, 2969, 2985	289, 822, 1190, 1379, 1388, 1468, 1469	995
C_2H_4	2989, 3026, 3103, 3106	826, 943, 949, 1023, 1236, 1342, 1444	1623
di-σ-bonded ethene	2887, 2896, 2987, 2992		
π-bonded ethene	3026, 3060		
Calculated values			
C_2H_6	2943, 2946, 3003, 3005, 3030, 3034	352, 787, 1173, 1333, 1343, 1467, 1468	982
C_2H_4	3037, 3051, 3114, 3144	791, 917, 928, 1031, 1196, 1337, 1411	1634
π-$H_2CH_2CIr_4$	2977, 2986, 3079, 3100	697, 781, 849, 945, 952, 1177, 1414, 1464	1165
di-σ-$H_2CH_2CIr_4$	2879, 2890, 2947, 2966	564, 659, 923, 993, 1064, 1199, 1362, 1387	1017

Table S4. C-H and C-C vibrational frequencies (in cm^{-1}; the theoretically obtained values have not been corrected) in the model adsorption complexes $C_2H_mIr_4H_n$ ($m = 2 / 4$, $n = 0, 3, 6, 9$) of ethene and ethyne.

Structure	C-H	C-C	Structure	C-H	C-C
Exp. [a]					
π-bonded ethene	3026, 3060				
di-σ-bonded ethene	2887, 2896, 2987, 2992				
Theory					
π-bonded ethene			π-bonded ethyne		
π-H$_2$CH$_2$CIr$_4$	2977, 2986, 3079, 3100	1165	π-HCHCIr$_4$	3131, 3181	1523
π-H$_2$CH$_2$CIr$_4$H	3002, 3011, 3085, 3111	1172			
π-H$_2$CH$_2$CIr$_4$H$_3$	2996, 3007, 3065, 3095	1148	π-HCHCIr$_4$H$_3$	3126, 3171	1519
π-H$_2$CH$_2$CIr$_4$H$_6$	2990, 3005, 3109, 3129	1193	π-HCHCIr$_4$H$_6$	3164, 3216	1569
π-H$_2$CH$_2$CIr$_4$H$_9$	3009, 3016, 3081, 3105	1155	π-HCHCIr$_4$H$_9$	3151, 3194	1582
π-H$_2$CH$_2$CIr$_4$H$_{10}$	3014, 3037, 3103, 3127	1198			
di-σ-bonded ethene			di-σ-bonded ethyne		
di-σ-H$_2$CH$_2$CIr$_4$	2879, 2890, 2947, 2966	1017	di-σ-HCHCIr$_4$	2912, 2945	1306
			di-σ-HCHCIr$_4$H$_2$	2946, 2968	1263
di-σ-H$_2$CH$_2$CIr$_4$H$_3$	2847, 2864, 2919, 2977	951	di-σ-HCHCIr$_4$H$_3$	2918, 3017	1320
di-σ-H$_2$CH$_2$CIr$_4$H$_6$	2775, 2917, 2929, 3020	952	di-σ-HCHCIr$_4$H$_6$	2944, 3036	1341
di-σ-H$_2$CH$_2$CIr$_4$H$_9$	2909, 2922, 3032, 3052	982	di-σ-HCHCIr$_4$H$_9$	3033, 3063	1367

[a] The experimental data are obtained in the investigation of ethene hydrogenation on Ir$_4$/γ-Al$_2$O$_3$ (H$_2$ pressure 300 Torr, C$_2$H$_4$ pressure 200−293 Torr), reported by Argo et al. The assignment of the bands in the experimental spectra is based on comparison with the vibrational modes of the corresponding molecules or fragments adsorbed on crystal metal surfaces.

Table S5. C-H and C-C vibrational frequencies (in cm^{-1}; the theoretically obtained values have not been corrected) in the model complexes $C_2H_mIr_4H_n$ ($m = 2 / 4$, $n = 0, 3, 6, 9$) of ethyl, ethylidyne, vinyl, and vinylidene.

Structure	CH$_2$	CH$_3$	C-C	Structure	CH	CH$_2$	C-C
Exp. [a]							
ethyl	2863	2929, 2957					
ethylydene		2896, 2947					
ethyl				vinyl			
				H_2CHCIr_4	2869	2898, 2959	1026
$H_3CH_2CIr_4H_3$	2850, 2899	2931, 3008, 3038	993	$H_2CHCIr_4H_3$	2815	2907, 2965	1030
$H_3CH_2CIr_4H_6$	2863, 2928	2934, 3010, 3038	994	$H_2CHCIr_4H_6$	2969	2911, 2994	1022
$H_3CH_2CIr_4H_9$	2915, 2978	2922, 2993, 3022	982	$H_2CHCIr_4H_9$	2927	2881, 2997	1057
ethylidyne				vinylidene			
H_3CCIr_4		2936, 3015, 3016	1115	H_2CCIr_4		2996, 3081	1140
H_3CCIr_4H		2941, 3021, 3029	1097	$H_2CCIr_4H_3$		3014, 3108	1208
$H_3CCIr_4H_2$		2933, 3009, 3017	1093	$H_2CCIr_4H_6$		3011, 3108	1255
$H_3CCIr_4H_3$		2935, 3012, 3019	1103	$H_2CCIr_4H_9$		3004, 3093	1175
$H_3CCIr_4H_4$		2931, 3011, 3015	1114				
$H_3CCIr_4H_6$		2936, 3013, 3042	1134				
$H_3CCIr_4H_9$		2934, 3002, 3029	1163				

[a] The experimental data are obtained in the investigation of ethene hydrogenation on Ir_4/γ-Al_2O_3 (H_2 pressure 300 Torr, C_2H_4 pressure 200−293 Torr), reported by Argo et al. The assignment of the bands in the experimental spectra is based on comparison with the vibrational modes of the corresponding molecules or fragments adsorbed on crystal metal surfaces.

S2. Electronic structure of $(C_2H_m)Ir_4H_n$ adsorption complexes.

Table S6. Characteristics of the electronic structure of iridium atoms in the model adsorption complexes $(C_2H_m)Ir_4$ ($m = 2, 3, 4$). Bold values correspond to iridium atoms to which the organic ligand is coordinated.

	π-C$_2$H$_4$	di-σ-C$_2$H$_4$	π-C$_2$H$_2$	di-σ-C$_2$H$_2$	H$_3$CC≡	H$_2$CHC–	H$_2$CC=
ΔE(Ir 4f) ^{a}							
Ir1	**0.83**	**0.82**	**1.44**	**0.73**	**0.60**	**1.10**	**1.02**
Ir2	0.13	**0.85**	0.18	**0.71**	**0.60**	**0.84**	**1.23**
Ir3	0.13	0.54	0.19	0.55	**0.60**	**0.65**	**0.89**
Ir4	-0.15	0.53	0.19	0.57	0.73	0.77	0.51
<Ir> ^{b}	0.04	0.53	0.18	0.56	0.73	0.77	0.51
<Ir(C)> ^{b}	**0.83**	**0.83**	**1.44**	**0.72**	**0.60**	**0.86**	**1.05**
PDC ^{c}							
Ir1	**0.30**	**0.10**	**0.51**	**0.33**	**0.06**	**0.09**	**0.18**
Ir2	0.11	**0.06**	0.04	**0.32**	**0.09**	**0.03**	**0.25**
Ir3	0.10	0.03	0.03	0.01	**0.06**	**0.08**	**0.28**
Ir4	-0.07	0.06	0.09	0.00	0.05	-0.02	-0.08
<Ir> ^{b}	0.05	0.04	0.05	0.01	0.05	-0.02	-0.08
<Ir(C)>	**0.30**	**0.08**	**0.51**	**0.32**	**0.07**	**0.07**	**0.24**

^{a} Shift of the average energy (in eV) of the Ir 4f core levels with respect to the bare cluster Ir$_4$. ^{b} Corresponding characteristics averaged over Ir atoms, not interacting with the organic ligand, or over Ir(C) atoms, interacting with the organic ligand. ^{c} Potential-derived charges of iridium atoms (in e).