Electronic Supplementary Material for Dalton Transactions

Supplementary Information

DFT calculations of d^0 M(NR)(CH*t*Bu)(X)(Y) (M = Mo, W ; R = CPh_3, 2,6-*i*Pr-C_6H_3; X and Y = CH_2*t*Bu, O*t*Bu, OSi(O*t*Bu)$_3$) olefin metathesis catalysts: structural, spectroscopic and electronic properties.

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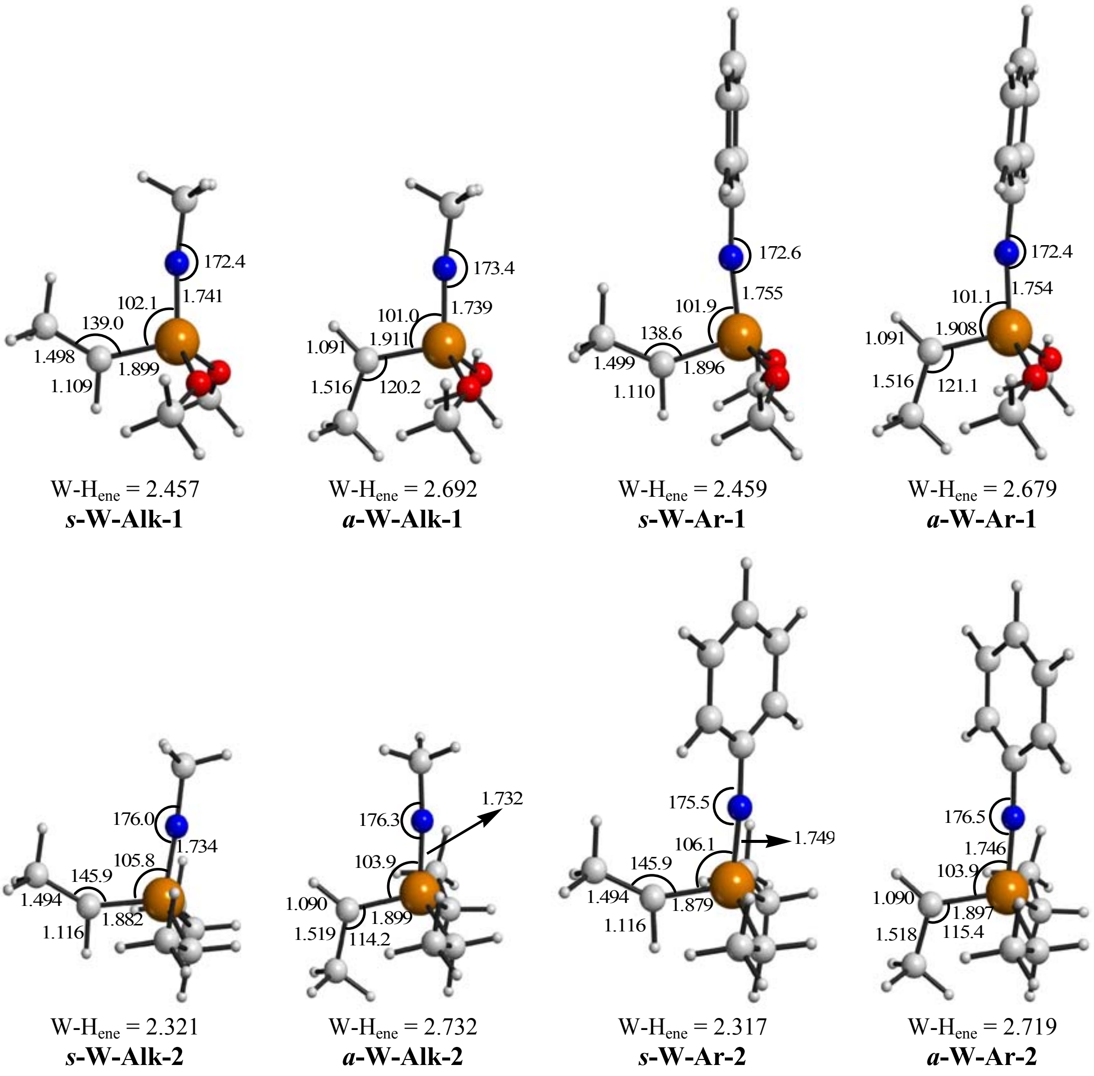
Table S1. NBO and AIM (in a.u.) analyses for *syn* isomers represented in Scheme 2. The three first lines gives the NPA charges on the metal (M), the carbon of the alkylidene (C_{ene}) and E. E is N for the imido group and C for the alkylidyne group. The next lines give the weights on C_{ene} (carbene) and E (imido, alkylidyne) in the M=C and M≡E bonds. ε, ρ, $\nabla^2\rho$ and H are respectivelly the ellipticity, the density, the Laplacian of the electron density and the energy at the bond critical point.

	***s*-Mo-Alk-1**	***s*-Mo-Ar-1**	***s*-Mo-Alk-2**	***s*-Mo-Ar-2**	***s*-Mo-Alk-3**	***s*-Mo-Ar-3**	***s*-W-Alk-1**	***s*-W-Ar-1**	***s*-W-Alk-2**	***s*-W-Ar-2**	***s*-Re-Alk-1**	***s*-Re-Alk-2**	***s*-Re-Alk-3**
M	1.38	1.28	1.08	1.11	1.17	1.20	1.68	1.72	1.40	1.39	1.17	0.80	0.95
C_{ene}	-0.46	-0.45	-0.42	-0.41	-0.40	-0.39	-0.60	-0.60	-0.55	-0.52	-0.47	-0.41	-0.40
E	-0.52	-0.52	-0.46	-0.48	-0.48	-0.49	-0.64	-0.66	-0.60	-0.57	-0.09	0.00	-0.05
$\%C_{\sigma(M=C)}$	64.3	60.4	60.9	60.7	64.8	62.3	65.3	63.7	63.1	62.7	60.0	58.1	60.1
$\%C_{\pi(M=C)}$	52.5	48.6	57.6	57.1	47.0	47.0	57.3	53.1	61.1	60.3	54.5	56.6	45.7
$\%E_{\sigma(M\equiv E)}$	75.2	74.6	74.2	74.9	76.7	76.2	76.4	76.4	75.2	75.7	62.5	59.9	61.2
$\%E_{\pi(M\equiv E)}$	78.4	71.6	76.7	75.7	76.6	71.5	80.0	74.4	78.5	75.9	52.1	52.7	42.6
$\%E_{\pi(M\equiv E)}$	63.2	62.8	64.5	68.1	64.8	64.0	66.4	67.6	67.9	71.9	38.5	38.3	41.8
$\varepsilon_{(M=C)}$	0.523	0.515	0.459	0.458	0.492	0.494	0.576	0.572	0.502	0.505	0.373	0.440	0.405
$\rho_{(M=C)}$	0.190	0.191	0.195	0.197	0.191	0.192	0.188	0.190	0.194	0.195	0.204	0.198	0.200
$\nabla^2\rho_{(M=C)}$	0.129	0.129	0.114	0.113	0.124	0.122	0.121	0.120	0.108	0.108	0.086	0.104	0.111
$H_{(M=C)}$	-0.120	-0.121	-0.122	-0.128	-0.120	-0.122	-0.122	-0.123	-0.128	-0.130	-0.139	-0.132	-0.134
$\varepsilon_{(M\equiv E)}$	0.008	0.001	0.014	0.024	0.032	0.022	0.006	0.019	0.022	0.031	0.017	0.021	0.016
$\rho_{(M\equiv E)}$	0.236	0.227	0.238	0.229	0.239	0.230	0.229	0.221	0.231	0.224	0.248	0.247	0.248
$\nabla^2\rho_{(M\equiv E)}$	0.699	0.684	0.706	0.687	0.696	0.676	0.689	0.670	0.691	0.671	0.306	0.334	0.319
$H_{(M\equiv E)}$	-0.163	-0.150	-0.164	-0.152	-0.166	-0.155	-0.162	-0.152	-0.165	-0.155	-0.200	-0.199	-0.199

Table S2. NBO and AIM (in a.u.) analyses for all transition states (see Scheme 2 for labelling). The three first lines gives the NPA charges on the metal (M), the carbon of the alkylidene (C_{ene}) and E. E is N for the imido group and C for the alkylidyne group. The next lines give the weights on C_{ene} (carbene) and E (imido, alkylidyne) in the M=C and M≡E bonds. ε, ρ, $\nabla^2\rho$ and H are respectivelly the ellipticity, the density, the Laplacian of the electron density and the energy at the bond critical point.

	***TS*-Mo-Alk-1**	**TS-Mo-Ar-1**	**TS-Mo-Alk-2**	**TS-Mo-Ar-2**	**TS-Mo-Alk-3**	**TS-Mo-Ar-3**	**TS-W-Alk-1**	**TS-W-Ar-1**	**TS-W-Alk-2**	**TS-W-Ar-2**	**TS-Re-Alk-1**	**TS-Re-Alk-2**	**TS-Re-Alk-3**
M	1.45	1.48	1.08	1.15	1.22	1.22	1.74	1.77	1.39	1.38	1.28	0.81	0.93
C_{ene}	-0.56	-0.55	-0.53	-0.54	-0.47	-0.43	-0.71	-0.69	-0.64	-0.63	-0.62	-0.59	-0.50
E	-0.59	-0.61	-0.52	-0.55	-0.47	-0.43	-0.67	-0.68	-0.62	-0.63	-0.25	-0.11	-0.09
$\%C_{\sigma(M=C)}$	62.8	61.1	63.6	64.2	63.4	58.0	64.9	64.2	65.8	65.9	62.7	63.1	60.4
$\%C_{\pi(M=C)}$	49.3	48.5	51.4	51.0	65.1	52.4	55.0	53.2	55.3	54.0	68.4	63.7	70.4
$\%E_{\sigma(M\equiv E)}$	68.4	67.9	66.9	69.3	79.9	63.9	68.7	68.8	69.1	70.2	35.8	66.3	66.9
$\%E_{\pi(M\equiv E)}$	61.3	62.6	62.4	63.0	62.4	65.3	66.3	67.6	65.6	65.6	60.6	38.4	39.2
$\%E_{\pi(M\equiv E)}$	LP	LP	LP	LP	76.5	LP	LP	LP	LP	LP	78.7	54.8	49.2
$\varepsilon_{(M=C)}$	0.535	0.532	0.445	0.455	0.392	0.406	0.546	0.561	0.453	0.468	0.433	0.350	0.192
$\rho_{(M=C)}$	0.188	0.188	0.186	0.186	0.197	0.200	0.184	0.185	0.185	0.186	0.189	0.190	0.197
$\nabla^2\rho_{(M=C)}$	0.106	0.103	0.131	0.128	0.153	0.145	0.100	0.099	0.128	0.123	0.078	0.082	0.140
$H_{(M=C)}$	-0.118	-0.110	-0.116	-0.116	-0.129	-0.133	-0.118	-0.119	-0.120	-0.120	-0.122	-0.123	-0.132
$\varepsilon_{(M\equiv E)}$	0.169	0.138	0.137	0.113	0.132	0.121	0.155	0.123	0.139	0.114	0.209	0.133	0.119
$\rho_{(M\equiv E)}$	0.258	0.215	0.230	0.219	0.234	0.224	0.226	0.217	0.226	0.218	0.281	0.231	0.234
$\nabla^2\rho_{(M\equiv E)}$	0.533	0.543	0.549	0.550	0.553	0.564	0.543	0.533	0.551	0.544	0.239	0.246	0.264
$H_{(M\equiv E)}$	-0.153	-0.139	-0.158	-0.143	-0.163	-0.149	-0.160	-0.149	-0.160	-0.149	-0.173	-0.176	-0.180



W-H_{ene} = 2.457
***s*-W-Alk-1**

W-H_{ene} = 2.692
***a*-W-Alk-1**

W-H_{ene} = 2.459
***s*-W-Ar-1**

W-H_{ene} = 2.679
***a*-W-Ar-1**

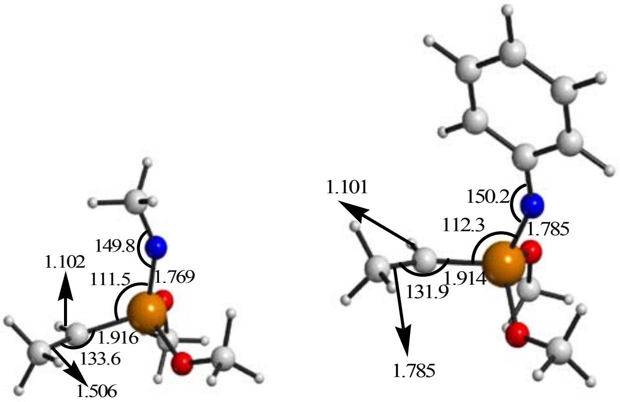
W-H_{ene} = 2.321
***s*-W-Alk-2**

W-H_{ene} = 2.732
***a*-W-Alk-2**

W-H_{ene} = 2.317
***s*-W-Ar-2**

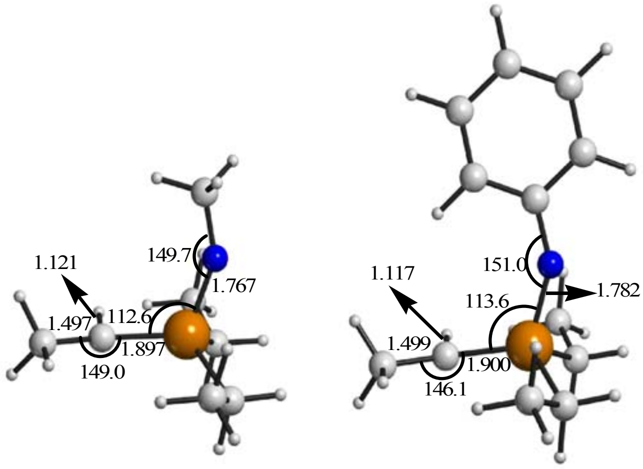
W-H_{ene} = 2.719
***a*-W-Ar-2**

Figure S1. DFT (B3PW91) optimized structures for *syn* (s) and *anti* (a) isomers of **W-Alk-1** to **W-Ar-2** complexes (Scheme 2.). Distances in Å and angles in degrees



W-H_{ene} = 2.530
TS-W-Alk-1

W-H_{ene} = 2.551
TS-W-Ar-1



W-H_{ene} = 2.265
TS-W-Alk-2

W-H_{ene} = 2.322
TS-W-Ar-2

Figure S2. DFT (B3PW91) optimized transition state structures for alkylidene rotation for **W-Alk-1** to **W-Ar-2** (Scheme 2). Distances in Å and angles in degrees