1,3-Metal-Carbon Bonding and Alkyne Metathesis: DFT Investigations on Model Complexes of Group 4, 5, and 6 Transition Metals

Cherumuttathu H. Suresh[*,‡,§] and Gernot Frenking[‡]

[‡]*Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany and* [§] *Chemical Sciences and Technology Division, National Institute for Interdisciplinary, Science and Technology, Trivandrum 695 019, India*

Supporting Information

Contents:

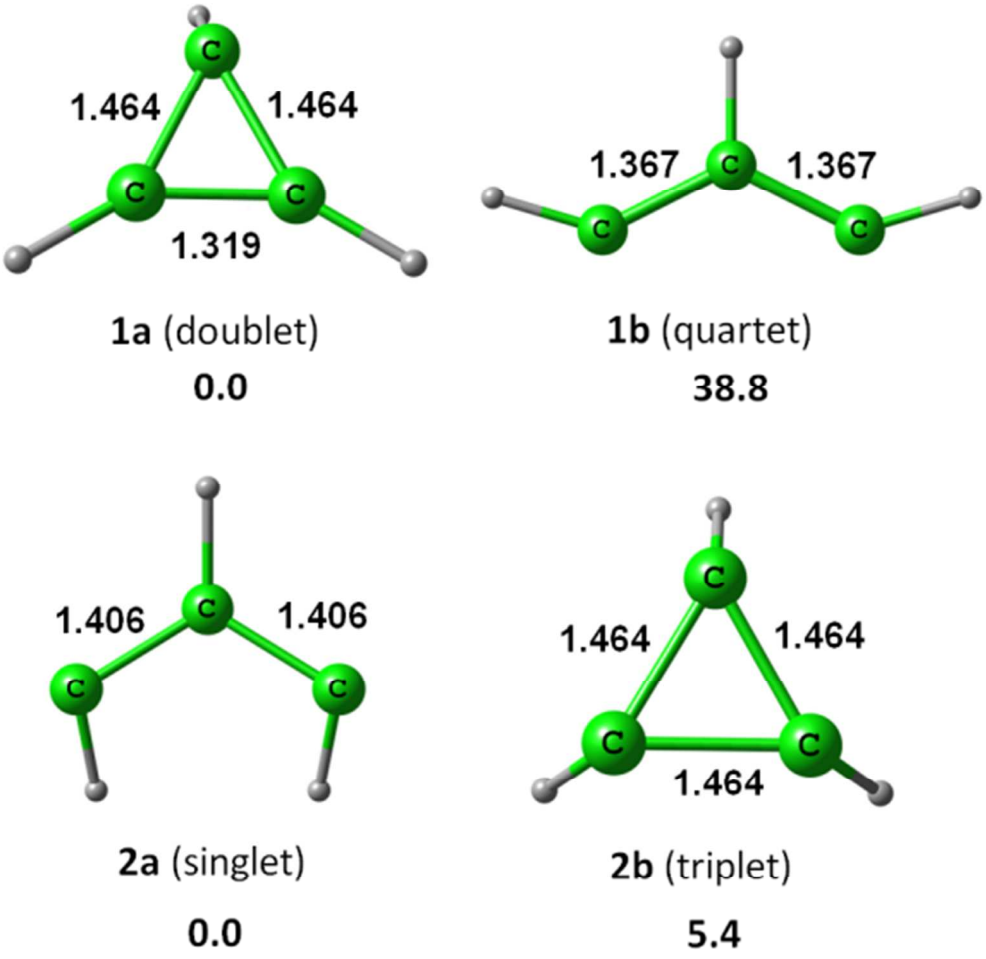


Figure S1. Optimized geometries of C_3H_3 and $C_3H_3^-$ fragments. Relative energy in kcal/mol and bond length in Å. BP86/def2-TZVPP level of DFT.

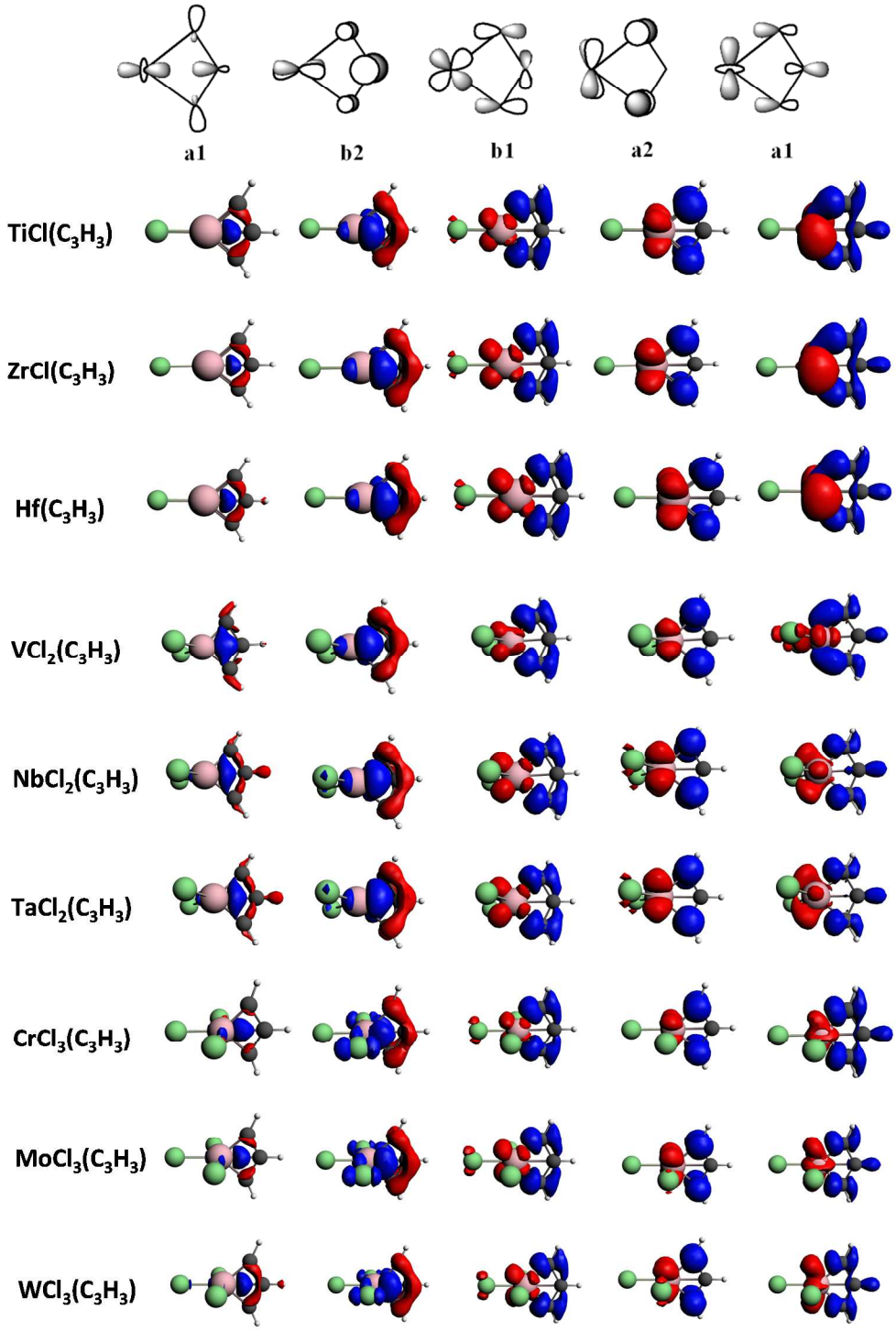


Figure S2. Top row: five main orbital interactions in $MCl_n(C_3H_3)$ complexes. Bottom rows: deformation density isosurface plots corresponding to the main orbital interactions listed in top row for $MCl_n(C_3H_3)$ complexes obtained using the ETS-NOCV calculations. Isosurface value of a_1 orbital in the first column is 0.002 a.u. and that for b_2 orbital in the second column is 0.001

a.u. For all other orbitals, isosurface value 0.003 a.u. is used. The ETS-NOCV method uses open-shell fragments and the deformation density plots given here are for the α-electrons. Very similar plots exist for β-electrons.

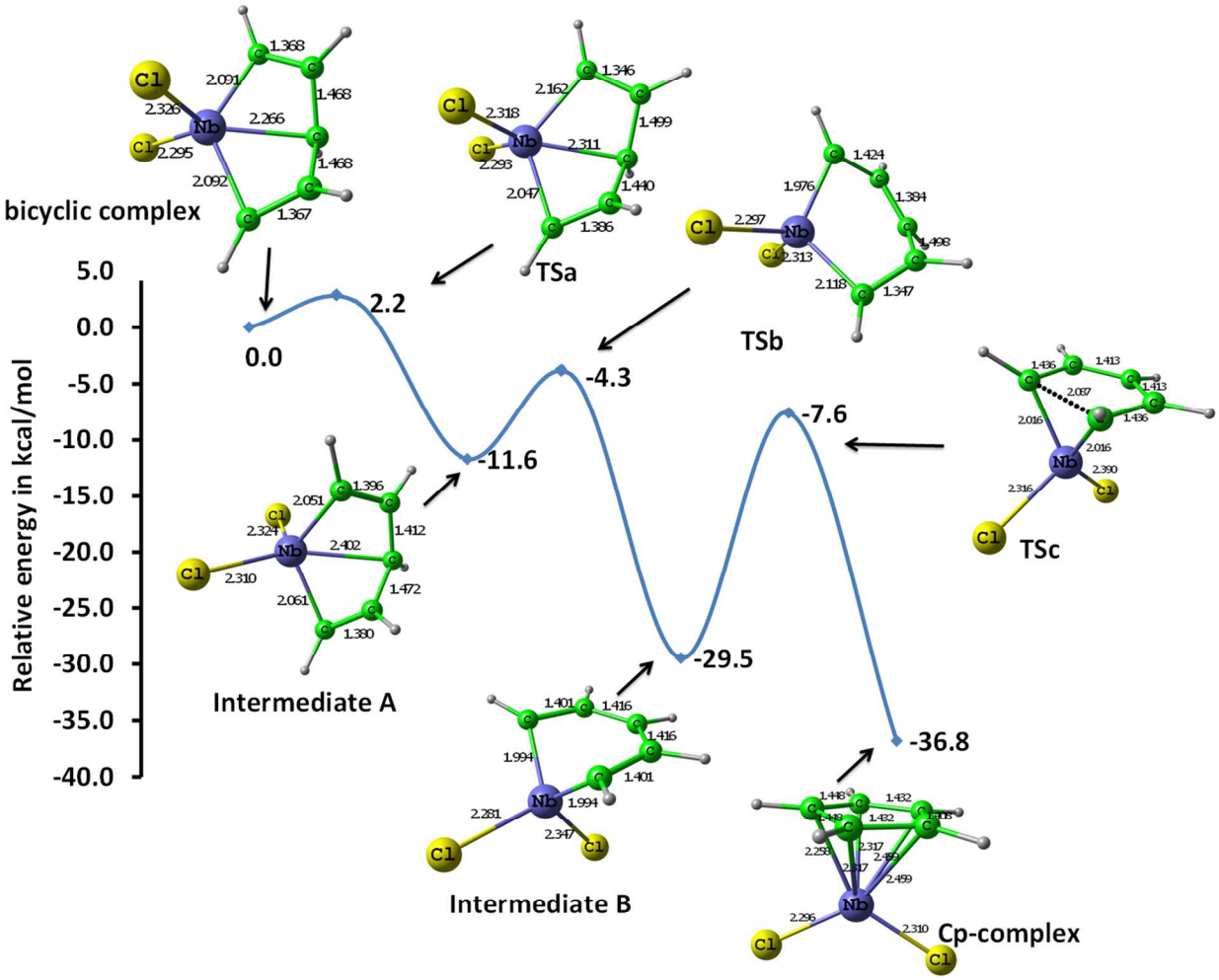


Figure S3. Rearrangement of the bicyclic complex to a more stable cyclopentadienyl-complex. BP86/def2-TZVPP level of DFT.

Table S1. Relative energy (kcal/mol) of $M(Cl)_n$ fragments (neutral or cation) in $MCl_n(C_3H_3)$ complexes. BP86/def2-TZVPP level of DFT.

M of $M(Cl)_n$ fragment	Doublet	Quartet	Singlet (cation)	Triplet (cation)
Ti	0.0	-3.5	0.0	-43.8
Zr	0.0	-3.3	0.0	-0.1
Hf	0.0	18.9	0.0	4.6
V	0.0	-16.7	0.0	-15.2
Nb	0.0	-12.3	0.0	-21.9
Ta	0.0	-10.9	0.0	-14.3
Cr	0.0	-18.1	0.0	-18.5
Mo	0.0	-22.6	0.0	-11.6
W	0.0	-15.5	0.0	-4.9

Table S2. Energy-decomposition analysis (BP86/TZ2P+) of the metal-carbon bonds of $MCl_n(C_3H_3)$ complexes for fragment pairs MCl_n and C_3H_3 (all energies in kcal/mol).

EDA Scheme	Energy	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W
Doublet	ΔE_{int}	-217.6	-224.6	-216.7	-233.7	-262.3	-261.2	-183.9	-220.1	-246.0
Singlet	ΔE_{int}	-344.0	-348.0	-380.8	-379.5	-396.1	-428.8	-372.9	-401.4	-415.4
Triplet	ΔE_{int}	-325.8	-342.0	-374.4	-338.2	-363.8	-395.0	-333.7	-363.3	-379.0
Doublet	ΔE_{Pauli}	214.1	251.4	310.2	281.9	271.0	495.2	249.9	278.5	359.2
Singlet	ΔE_{Pauli}	317.0	353.7	383.6	362.4	417.2	456.2	469.3	515.5	326.8
Triplet	ΔE_{Pauli}	343.8	390.6	438.1	377.2	436.6	489.5	464.3	524.5	484.3
Doublet	ΔE_{ele}	-106.2	-131.7	-180.8	-122.5	-146.3	-308.0	-96.1	-118.4	-194.7
Singlet	ΔE_{ele}	-363.5	-396.2	-445.6	-397.7	-447.1	-502.3	-460.6	-509.7	-292.6
Triplet	ΔE_{ele}	-386.8	-436.9	-501.3	-398.1	-461.8	-529.1	-443.2	-507.3	-448.1
Doublet	ΔE_{orb}	-325.6	-344.3	-346.0	-393.1	-387.1	-448.5	-337.7	-380.2	-410.5
Singlet	ΔE_{orb}	-297.4	-305.5	-318.9	-344.3	-366.2	-382.7	-381.6	-407.1	-449.6
Triplet	ΔE_{orb}	-282.9	-295.7	-311.2	-317.2	-338.5	-355.4	-354.8	-380.5	-415.1
Doublet	ΔE_{a1}	-189.7	-193.7	-190.6	-264.4	-204.8	-261.6	-161.8	-178.7	-198.1
Singlet	ΔE_{a1}	-63.8	-65.0	-71.3	-95.1	-94.5	-102.0	-118.9	-122.0	-169.9
Triplet	ΔE_{a1}	-63.8	-64.7	-70.6	-94.1	-93.1	-99.0	-118.3	-120.1	-129.9
Doublet	ΔE_{a2}	-56.7	-64.1	-69.5	-62.0	-69.6	-76.4	-41.7	-56.4	-64.4
Singlet	ΔE_{a2}	-126.5	-128.6	-137.8	-106.3	-123.6	-135.4	-64.0	-84.5	-82.6
Triplet	ΔE_{a2}	-54.2	-58.4	-62.9	-56.5	-65.8	-70.6	-52.5	-59.3	-83.0
Doublet	ΔE_{b1}	-62.5	-67.7	-66.2	-54.2	-91.5	-87.7	-107.7	-116.2	-116.8
Singlet	ΔE_{b1}	-84.7	-88.0	-85.6	-112.9	-118.4	-114.6	-159.8	-158.0	-150.2
Triplet	ΔE_{b1}	-140.4	-146.7	-151.8	-135.8	-149.1	-154.4	-145.2	-159.3	-156.7
Doublet	ΔE_{b2}	-16.6	-18.8	-19.7	-12.5	-21.3	-22.8	-26.4	-29.0	-31.2
Singlet	ΔE_{b2}	-22.5	-23.9	-24.3	-29.9	-29.7	-30.7	-39.0	-42.6	-46.8
Triplet	ΔE_{b2}	-24.5	-25.9	-25.9	-30.8	-30.6	-31.4	-38.9	-41.8	-45.5
Doublet	ΔE_{prep}	87.8	82.5	77.9	109.6	101.3	99.0	161.4	145.8	143.8

Singlet	ΔE_{prep}	48.9	45.5	75.1	76.4	74.2	91.4	129.7	123.7	122.6
Triplet	ΔE_{prep}	25.8	34.9	64.1	28.3	36.6	52.2	74.8	80.1	80.0
Doublet	$-D_e$	-129.8	-142.1	-138.8	-124.1	-161.0	-162.2	-22.5	-74.3	-102.2
Singlet	$-D_e$	-295.1	-302.5	-305.7	-303.1	-321.9	-337.4	-243.2	-277.7	-292.8
Triplet	$-D_e$	-300.0	-307.1	-310.4	-309.9	-327.2	-342.7	-258.9	-283.2	-298.9

Table S3. Electron density (in e/Å^3) at the (3, -1) bond critical points (bcp) for M-C_α and C_α-C_β bonds and (3, +1) ring critical point (rcp) observed between M and C_β. Calculations are done at BP86/TZVPP level for metallacyclobutadiene complexes given in Figure 1a.

Complex	Electron density at		
	M-C_α bcp	M-C_β rcp	C_α-C_β bcp
$TiCl(C_3H_3)$	0.139	0.076	0.276
$ZrCl(C_3H_3)$	0.128	0.071	0.272
$HfCl(C_3H_3)$	0.126	0.071	0.273
$VCl_2(C_3H_3)$	0.162	0.085	0.281
$NbCl_2(C_3H_3)$	0.156	0.082	0.273
$TaCl_2(C_3H_3)$	0.153	0.080	0.273
$CrCl_3(C_3H_3)$	0.176	0.088	0.289
$MoCl_3(C_3H_3)$	0.174	0.090	0.279
$WCl_3(C_3H_3)$	0.174	0.089	0.276

Cartesian coordinates for all the complexes optimized at BP86/def2-TZVPP level and SCF energies

1a. 1,3-MC bonded metallacyclobutadienes (Figure 1a)

Ti complex

E = -1426.01389974 a.u.

Ti	-0.035046000	-0.000175000	-0.001512000
Cl	2.227556000	0.000006000	0.000982000
C	-1.430797000	-1.267624000	0.000508000
C	-2.118916000	0.000254000	0.001250000
C	-1.430277000	1.267802000	-0.000470000
H	-2.002931000	-2.194331000	0.000889000
H	-3.213128000	0.000417000	0.003674000
H	-2.001450000	2.195068000	0.004273000

1,3-MC bonded Zr complex

E = -623.553585467 a.u.

Zr	0.026668000	-0.000149000	-0.328131000
Cl	-2.281020000	0.000104000	0.357211000
C	1.491441000	-1.285285000	0.201359000
C	2.110155000	0.000389000	0.450917000
C	1.491304000	1.285479000	0.200999000
H	2.024404000	-2.182219000	0.513725000
H	3.105582000	-0.000227000	0.906175000
H	2.023228000	2.183146000	0.513095000

1,3-MC bonded Hf complex

E= -624.524484565 a.u.

Hf	-0.015963000	-0.000299000	-0.263525000
Cl	2.248868000	0.000497000	0.509781000
C	-1.465901000	-1.275694000	0.349261000
C	-2.083492000	0.000864000	0.613893000
C	-1.465574000	1.276515000	0.347839000
H	-1.958940000	-2.185731000	0.682288000
H	-3.075100000	0.001010000	1.079929000
H	-1.957553000	2.187657000	0.679362000

1,3-MC bonded V complex

E = -1980.90342444 a.u.

V	-0.092981000	-0.000034000	0.000000000
Cl	1.142126000	1.790287000	-0.000004000
Cl	1.143184000	-1.789629000	0.000002000
C	-1.416927000	-0.000414000	-1.247259000
C	-2.118524000	-0.000598000	-0.000001000
C	-1.416915000	-0.000406000	1.247262000
H	-1.892877000	-0.000541000	-2.223623000
H	-3.211760000	-0.000877000	0.000013000
H	-1.892874000	-0.000493000	2.223622000

1,3-MC bonded Nb complex

E = -1093.85335848 a.u.

Nb	-0.068445000	-0.000188000	-0.000288000
Cl	1.236248000	1.910264000	0.000037000
Cl	1.243612000	-1.905583000	0.000041000
C	-1.543977000	-0.003057000	-1.271143000
C	-2.225001000	-0.003654000	0.000682000
C	-1.542242000	-0.003031000	1.271818000
H	-2.084562000	-0.004032000	-2.213405000
H	-3.317652000	-0.005330000	0.001125000
H	-2.081846000	-0.004049000	2.214653000

1,3-MC bonded Ta complex

E = -1093.91321624 a.u.

Ta	0.048240000	-0.000025000	-0.000290000
Cl	-1.262078000	-1.911091000	0.000190000
Cl	-1.260795000	1.911916000	0.000191000
C	1.543582000	-0.000502000	-1.269634000
C	2.228574000	-0.000646000	0.000895000
C	1.541720000	-0.000508000	1.270643000
H	2.082757000	-0.000671000	-2.211347000
H	3.321602000	-0.000945000	0.001577000
H	2.079741000	-0.000666000	2.213021000

1,3-MC bonded Cr complex

E = -2541.59164869 au

Cr	-0.092791000	-0.144258000	0.048467000
Cl	-2.202669000	-0.085184000	-0.591563000
Cl	2.167441000	0.336441000	-0.454460000
Cl	-0.140178000	2.018320000	0.398297000
C	0.495666000	-1.635279000	-0.778087000
C	0.306381000	-2.045796000	0.566251000
C	-0.122578000	-1.087515000	1.540726000
H	0.952219000	-2.197465000	-1.586062000
H	0.520766000	-3.076729000	0.867429000
H	-0.340921000	-1.234859000	2.593444000

1,3-MC bonded Mo complex

E = -1565.33366451 au

Mo	0.000187000	-0.101355000	0.000651000
Cl	-2.353012000	0.166580000	-0.005395000
Cl	2.353115000	0.170850000	-0.006467000
Cl	-0.002655000	2.209266000	0.004228000
C	0.000072000	-1.532864000	-1.249199000
C	0.002449000	-2.231011000	0.005870000
C	0.002932000	-1.525954000	1.257235000
H	-0.005175000	-1.993176000	-2.232180000
H	0.003596000	-3.323857000	0.008485000
H	0.004380000	-1.980900000	2.242672000

1,3-MC bonded W complex

E = -1564.25860652 au

W	0.000018000	-0.078353000	0.000019000
Cl	-2.352035000	0.195145000	-0.000232000
Cl	2.351933000	0.197293000	-0.000044000
Cl	-0.001174000	2.246977000	0.000046000
C	0.000930000	-1.530649000	-1.256482000
C	0.001133000	-2.231094000	0.000056000
C	0.000526000	-1.530186000	1.256711000
H	0.002477000	-1.998593000	-2.234512000
H	0.001854000	-3.323586000	0.000558000
H	0.000474000	-1.998197000	2.234712000

1b. η^3- complexes (Figure 1b)

η^3- complex of Ti

E = -1425.97562932 a.u.

Ti	-0.000476000	0.000335000	-0.000192000
Cl	-2.298848000	-0.000128000	0.000097000
C	1.749370000	-0.337831000	0.812809000
C	1.749946000	0.872591000	-0.113983000
C	1.749428000	-0.535429000	-0.698484000
H	2.532271000	-0.626990000	1.509427000
H	2.533705000	1.619607000	-0.211508000
H	2.532436000	-0.993796000	-1.297389000

η^3- complex of Zr

E = -623.508203327 a.u.

Zr	-0.000267000	-0.000752000	-0.000871000
Cl	2.463235000	0.000675000	0.000804000
C	-1.869821000	-0.008565000	0.900356000
C	-1.871830000	-0.773865000	-0.457123000
C	-1.870380000	0.784767000	-0.440695000
H	-2.728997000	-0.015388000	1.567810000
H	-2.732960000	-1.346357000	-0.795119000
H	-2.730167000	1.366322000	-0.766735000

η^3- complex of Hf

E = -624.472593316 a.u.

Hf	-0.004547000	0.000383000	-0.000369000
Cl	2.452604000	-0.000650000	0.000627000
C	-1.841759000	-0.629978000	-0.671568000
C	-1.842363000	0.896287000	-0.208020000
C	-1.841106000	-0.268424000	0.881612000
H	-2.738516000	-1.051509000	-1.121199000
H	-2.739727000	1.495820000	-0.347043000
H	-2.737250000	-0.448163000	1.472030000

η^3- complex of V

E -1980.85843542 au

V	0.015660000	-0.055939000	0.000164000
Cl	-1.851358000	-1.208687000	-0.000084000
C	0.218982000	1.657335000	0.820307000
C	-0.934951000	1.802335000	-0.000445000
C	0.219781000	1.657268000	-0.820051000

H	0.806735000	2.310322000	1.466110000
H	-1.947253000	2.188435000	-0.000791000
H	0.807908000	2.310089000	-1.465674000
Cl	2.024861000	-0.922128000	-0.000051000

η^3- complex of Nb

E = -1093.79435459 au

Nb	-0.020539000	-0.067857000	0.000076000
Cl	1.984716000	-1.258407000	-0.000087000
C	-0.180599000	1.770354000	-0.842364000
C	0.978399000	1.884636000	-0.000656000
C	-0.179331000	1.770310000	0.842941000
H	-0.738930000	2.495727000	-1.437381000
H	1.965875000	2.331609000	-0.001205000
H	-0.737183000	2.496020000	1.438047000
Cl	-2.182275000	-0.923534000	-0.000038000

η^3- complex of Ta

E = -1093.84681889 au

Ta	0.035416000	-0.030928000	-0.000013000
Cl	-1.764385000	-1.518876000	0.000005000
C	-0.129584000	1.810869000	0.854132000
C	-1.287487000	1.751287000	-0.000052000
C	-0.129161000	1.810881000	-0.854019000
H	0.292600000	2.620625000	1.453281000
H	-2.328293000	2.052814000	-0.000492000
H	0.292769000	2.621095000	-1.452727000
Cl	2.260559000	-0.673773000	0.000025000

η^3- complex of Cr

E = -2541.63616575 au

Cr	0.054739000	-0.000216000	0.000568000
Cl	-0.842880000	-0.105697000	1.964786000
C	1.867626000	-0.699676000	-0.429536000
C	1.853572000	-0.052515000	0.849883000
C	1.871600000	0.731852000	-0.350434000
H	2.282098000	-1.539277000	-0.972125000
H	2.251610000	-0.109074000	1.854571000
H	2.290763000	1.623939000	-0.797114000
Cl	-0.810013000	-1.653658000	-1.091810000
Cl	-0.799754000	1.768274000	-0.903472000

η^3- complex of Mo

E = -1565.35129466 au

Mo	-0.054535000	-0.000865000	-0.000275000
Cl	0.881435000	-0.072010000	2.079269000
C	-1.957182000	0.718943000	-0.386196000
C	-1.943341000	-0.059685000	0.843996000
C	-1.938647000	-0.734881000	-0.445851000
H	-2.474022000	1.561345000	-0.828327000
H	-2.449778000	-0.104584000	1.799946000
H	-2.436501000	-1.550345000	-0.955227000

Cl	0.849510000	1.855533000	-0.969565000
Cl	0.897631000	-1.749189000	-1.114207000

η^3- complex of W
E = -1564.25985797 au

W	0.060653000	0.000201000	0.000359000
Cl	-0.944218000	-0.104441000	2.059998000
C	1.953799000	-0.712468000	-0.442035000
C	1.940439000	-0.040964000	0.866017000
C	1.952529000	0.755497000	-0.370259000
H	2.521029000	-1.490551000	-0.937722000
H	2.497611000	-0.085423000	1.793646000
H	2.520234000	1.579099000	-0.785369000
Cl	-0.911550000	-1.741422000	-1.132138000
Cl	-0.915281000	1.844077000	-0.952531000

1c. Metallacycloobutadienes of group 6 metals with no 1,3-MC bonding (structures in Figure 1c)
Cr complex
E = -2541.59970623 au

Cr	0.054355000	-0.132973000	0.000134000
Cl	-0.889766000	-0.877874000	-1.758589000
Cl	-0.848015000	1.919023000	-0.000609000
Cl	-0.889237000	-0.877218000	1.759314000
C	1.728130000	1.073932000	0.000464000
C	2.598675000	0.028866000	-0.000526000
C	1.668023000	-1.043364000	-0.000556000
H	1.851720000	2.155541000	0.001025000
H	3.697986000	0.018243000	-0.001144000
H	1.836123000	-2.125845000	-0.001370000

Mo complex
E = -1565.32747960 au

Mo	-0.065667000	0.006338000	-0.143768000
Cl	0.926744000	-1.853015000	-0.941829000
Cl	0.939789000	-0.073908000	1.979254000
Cl	0.942419000	1.907116000	-0.812791000
C	-1.740307000	-0.032094000	1.160963000
C	-2.660019000	0.001126000	0.151523000
C	-1.816983000	0.041528000	-1.006304000
H	-1.842287000	-0.068926000	2.243450000
H	-3.759178000	-0.003140000	0.204764000
H	-2.088850000	0.079224000	-2.065826000

W complex
E = -1564.24411561 au

W	0.070379000	0.107105000	0.062372000
Cl	-0.179924000	-1.438758000	1.720522000
Cl	-1.240997000	-1.204784000	-1.426663000
Cl	-1.348969000	1.861228000	0.162049000
C	1.429230000	-0.240787000	-1.472376000
C	2.474785000	0.186866000	-0.685882000
C	1.856983000	0.852520000	0.428514000
H	1.415653000	-0.810050000	-2.397651000

H 3.549139000 -0.021176000 -0.814608000
H 2.349302000 1.413230000 1.224742000

1d. Structures given in Figure 4.

Alkylidyne Ti complex
E = -1348.51027039 au
Ti 0.603931000 -0.473826000 0.000023000
Cl -1.537620000 0.231594000 -0.000032000
C 1.760527000 0.788827000 0.000001000
H 2.289887000 1.754122000 0.000028000

Alkylidyne Zr complex
E = -546.044719412 au
Zr -0.491067000 -0.344654000 0.000018000
Cl 1.817276000 0.270245000 -0.000007000
C -1.551400000 1.166328000 -0.000262000
H -1.942605000 2.194037000 0.000963000

Alkylidyne Hf complex
E = -546.999469733 au
Hf -0.325691000 -0.213787000 0.000002000
Cl 1.981043000 0.303551000 -0.000001000
C -1.415874000 1.311665000 -0.000040000
H -1.732736000 2.362311000 0.000149000

Alkylidyne V complex
E = -1903.41526417 au
V -0.000003000 0.343987000 -0.371050000
Cl -1.873025000 -0.636437000 0.161621000
Cl 1.873000000 -0.636474000 0.161617000
C 0.000082000 1.829883000 0.348353000
H 0.000003000 2.748481000 0.949002000

Alkylidyne Nb complex
E = -1016.35227270 au
Nb -0.000003000 0.352078000 -0.338350000
Cl -1.911376000 -0.813033000 0.237578000
Cl 1.911264000 -0.813205000 0.237532000
C 0.000249000 1.775637000 0.718277000
H 0.000555000 2.557016000 1.485799000

Alkylidyne Ta complex
E = -1016.39267686 au
Ta 0.000005000 0.277009000 -0.227245000
Cl -1.887899000 -0.955403000 0.271293000
Cl 1.887825000 -0.955496000 0.271271000
C 0.000078000 1.651325000 0.932848000
H 0.000389000 2.355699000 1.768188000

Alkylidyne Cr complex
E = -2464.22014910 au
Cr -0.077202000 0.159478000 0.000000000
Cl -0.777397000 -0.765129000 1.789035000

Cl	-0.777397000	-0.765129000	-1.789035000
Cl	2.011960000	0.585630000	0.000000000
C	-0.777397000	1.606472000	0.000000000
H	-1.254580000	2.592395000	0.000000000

Alkylidyne Mo complex
E = -1487.94352352 au

Mo	-0.062496000	0.129293000	0.000000000
Cl	-0.814989000	-0.835056000	1.901164000
Cl	-0.814989000	-0.835056000	-1.901164000
Cl	2.148082000	0.601888000	0.000000000
C	-0.814989000	1.678183000	0.000000000
H	-1.293026000	2.660381000	0.000000000

Alkylidyne W complex
E = -1486.85279778 au

W	-0.050201000	0.106642000	0.000000000
Cl	-0.801652000	-0.876132000	1.903745000
Cl	-0.801652000	-0.876132000	-1.903745000
Cl	2.179462000	0.534192000	0.000000000
C	-0.801652000	1.690231000	0.000000000
H	-1.269873000	2.674316000	0.000000000

Metathesis transition state for Ti (Figure 4)
E = -1425.88739526 au

Ti	0.037986000	0.564858000	-0.407448000
Cl	-1.770444000	-0.737463000	0.059832000
C	0.217546000	1.904944000	0.651107000
C	1.656481000	-1.237451000	0.634656000
C	2.305531000	-0.757727000	-0.271024000
H	0.159272000	2.661075000	1.449971000
H	1.060765000	-1.659973000	1.422800000
H	2.964478000	-0.349699000	-1.014488000

Metathesis transition state for Zr (Figure 4)
E = -623.422783563 au

Zr	-0.066391000	-0.545553000	-0.331777000
Cl	1.832301000	0.874086000	0.112364000
C	-0.334490000	-1.692100000	1.097965000
C	-1.501227000	1.713259000	0.543927000
C	-2.225588000	1.044753000	-0.166132000
H	-0.317988000	-2.224082000	2.061030000
H	-0.823830000	2.283732000	1.151582000
H	-2.983832000	0.507557000	-0.706280000

Metathesis transition state for Hf (Figure 4)
E = -624.379363052 au

Hf	-0.030670000	-0.325515000	-0.192136000
Cl	1.869339000	1.073689000	0.155420000
C	-0.103994000	-1.742487000	1.061552000
C	-1.995813000	1.736578000	0.614556000
C	-2.097796000	0.836193000	-0.231057000
H	0.051812000	-2.406421000	1.921634000

H	-1.696945000	2.557160000	1.240407000
H	-2.739795000	0.051920000	-0.640678000

Metathesis transition state for V (Figure 4)
E = -1980.80258652 au

V	0.000070000	-0.067499000	0.228459000
Cl	-1.933118000	-0.893338000	-0.419754000
Cl	1.933849000	-0.892075000	-0.419799000
C	0.000001000	-0.017100000	1.880157000
C	0.606517000	2.285553000	-0.373717000
C	-0.608527000	2.285342000	-0.373842000
H	0.000026000	-0.063706000	2.976908000
H	1.680136000	2.323087000	-0.377167000
H	-1.682162000	2.322358000	-0.377469000

Metathesis transition state for Nb (Figure 4)
E = -1093.73957672 au

Nb	-0.000203000	-0.019549000	0.171796000
Cl	-2.026082000	-0.997675000	-0.454991000
Cl	2.023398000	-1.002498000	-0.454788000
C	-0.000193000	0.032261000	1.947426000
C	0.611259000	2.468732000	-0.450975000
C	-0.603359000	2.470723000	-0.451202000
H	-0.000306000	-0.036005000	3.040735000
H	1.686534000	2.502201000	-0.444510000
H	-1.678512000	2.507941000	-0.445107000

Metathesis transition state for Ta (Figure 4)
E = -1093.78271272 au

Ta	-0.000672000	-0.005385000	0.124032000
Cl	-2.016488000	-1.022066000	-0.469162000
Cl	2.001574000	-1.049321000	-0.467629000
C	-0.000051000	0.165056000	1.917274000
C	0.629358000	2.451689000	-0.547528000
C	-0.586106000	2.460758000	-0.547817000
H	-0.000421000	0.155666000	3.010367000
H	1.705101000	2.479463000	-0.535021000
H	-1.661263000	2.506500000	-0.535840000

Metathesis transition state for Cr (Figure 4)
E = -2541.56240074 au

Cr	-0.127991000	0.000000000	0.151273000
Cl	0.201143000	2.075435000	-0.486661000
Cl	0.201143000	-2.075435000	-0.486661000
Cl	-2.279970000	0.000000000	-0.029821000
C	0.061349000	0.000000000	1.753779000
C	2.544218000	0.000000000	0.607633000
C	2.352167000	0.000000000	-0.595094000
H	0.118918000	0.000000000	2.847881000
H	2.815670000	0.000000000	1.643295000
H	2.311422000	0.000001000	-1.666210000

Metathesis transition state for Mo (Figure 4)

E = -1565.30009569 au

Mo	0.022873000	-0.000253000	0.124345000
Cl	-0.166147000	-2.231990000	-0.525460000
Cl	-0.100988000	2.235959000	-0.525326000
Cl	2.308747000	-0.033819000	0.036190000
C	-0.378835000	0.005812000	1.819118000
C	-2.501428000	0.035595000	0.464853000
C	-2.115899000	0.031216000	-0.712311000
H	-0.585614000	0.008850000	2.891959000
H	-2.834801000	0.039348000	1.482764000
H	-2.270661000	0.034135000	-1.779032000

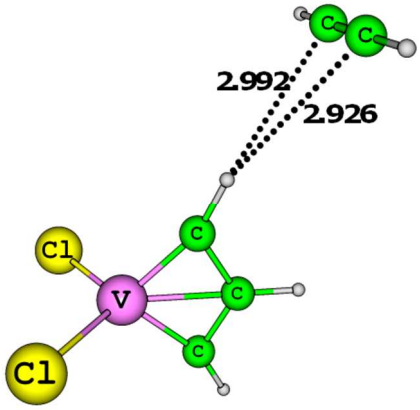
Metathesis transition state for W (Figure 4)

E = -1564.21890111 au

W	-0.000002000	-0.020356000	0.089333000
Cl	2.253794000	-0.025923000	-0.557753000
Cl	-2.253807000	-0.025904000	-0.557726000
Cl	0.000014000	2.288460000	0.112565000
C	0.000036000	-0.613243000	1.772198000
C	0.000000000	-2.457632000	0.376867000
C	-0.000003000	-2.002036000	-0.801333000
H	0.000069000	-0.927694000	2.815853000
H	0.000013000	-2.844469000	1.377253000
H	-0.000155000	-2.306799000	-1.840610000

1e. Structures given in Figure 5 for the metathesis mechanism using V complex

Initial van der Waals complex

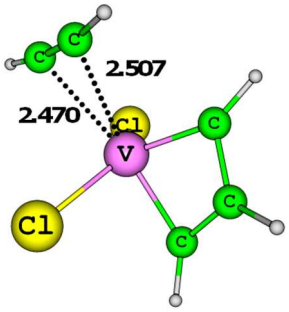


E = -2058.26186400 au

V	0.812243000	-0.015144000	0.159305000
Cl	1.575143000	1.894927000	-0.554526000
Cl	1.818986000	-1.667860000	-0.837448000
C	-1.000767000	-0.138029000	0.173068000
C	-0.637236000	-0.221277000	1.556322000
C	0.730186000	-0.162672000	1.971129000
H	-2.024033000	-0.175743000	-0.194958000
H	-1.425482000	-0.331273000	2.305788000
H	1.067462000	-0.220025000	3.002055000
H	-4.689701000	1.686878000	-0.548460000

C	-4.818777000	0.623811000	-0.529071000
C	-4.972357000	-0.574491000	-0.514320000
H	-5.116316000	-1.635708000	-0.507648000

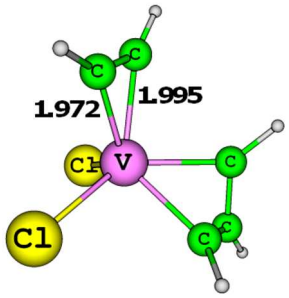
Transition state for acetylene coordination



E = -2058.22253800 au

V	0.037258000	-0.147275000	-0.025708000
Cl	-1.400358000	1.356660000	-0.905559000
Cl	1.934187000	-0.851008000	-0.856007000
C	-1.460357000	-1.363942000	-0.510700000
C	-1.491401000	-1.562726000	0.853980000
C	-0.259518000	-1.161193000	1.487320000
H	-2.311588000	-1.436325000	-1.188590000
H	-2.394426000	-1.834253000	1.429332000
H	0.137496000	-1.533772000	2.431043000
C	0.663882000	1.563334000	1.696295000
C	1.304949000	1.846718000	0.695270000
H	0.165897000	1.464663000	2.639222000
H	1.925271000	2.197784000	-0.106074000

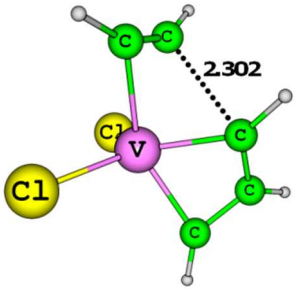
Complex formed with acetylene



E = -2058.25280648 au

V	-0.007163000	0.049234000	0.173846000
Cl	0.548205000	1.768289000	-1.077965000
Cl	-2.031725000	-0.627905000	-0.668646000
C	-0.943685000	0.339294000	1.884834000
C	0.222043000	0.896299000	1.965749000
C	1.690166000	-0.928313000	0.647555000
H	-1.898468000	0.134496000	2.361338000
H	0.883000000	1.470164000	2.613215000
H	2.303450000	-1.141606000	1.524335000
C	1.898170000	-1.307537000	-0.673570000
C	0.667192000	-1.799854000	-0.320010000
H	2.673282000	-1.391779000	-1.432274000
H	0.220008000	-2.789525000	-0.400028000

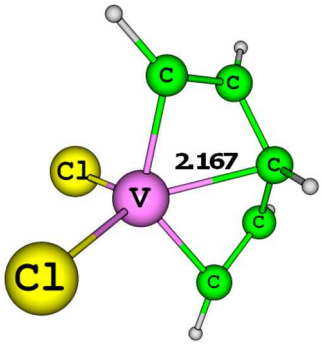
Transition state of CC bond coupling



E = -2058.23280647 au

V	-0.057228000	-0.101531000	-0.065445000
Cl	0.471976000	2.061113000	-0.053604000
Cl	-2.169437000	-0.339738000	-0.643625000
C	-0.678390000	-0.662972000	1.908973000
C	0.455076000	-0.125842000	2.060290000
C	1.358981000	-1.384233000	0.357881000
H	-1.651529000	-0.972309000	2.264042000
H	1.216632000	0.380126000	2.638504000
H	1.682818000	-2.082660000	1.126777000
C	2.024795000	-0.971753000	-0.820886000
C	0.974555000	-0.683649000	-1.664636000
H	3.103840000	-0.827805000	-0.986669000
H	1.011208000	-0.454819000	-2.734268000

Bicyclic product

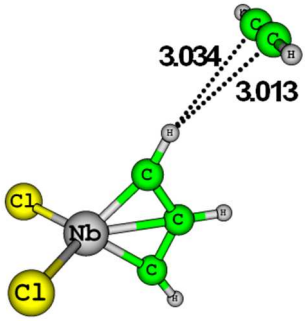


E = -2058.29627423 au

V	-0.173031000	-0.067863000	0.000612000
Cl	-0.196306000	2.134285000	-0.003685000
Cl	-2.176449000	-0.869513000	0.001300000
C	0.506108000	-0.510047000	1.794457000
C	1.762617000	-0.412575000	1.283221000
C	1.721873000	-1.118353000	0.001920000
H	0.098034000	-0.191359000	2.757056000
H	2.578612000	0.246800000	1.612874000
H	1.416451000	-2.160676000	0.004693000
C	1.762264000	-0.419015000	-1.283210000
C	0.505177000	-0.517994000	-1.792152000
H	2.579374000	0.236413000	-1.617927000
H	0.095845000	-0.203577000	-2.755644000

1f. Structures given in Figure 5 for the metathesis mechanism using Nb complex

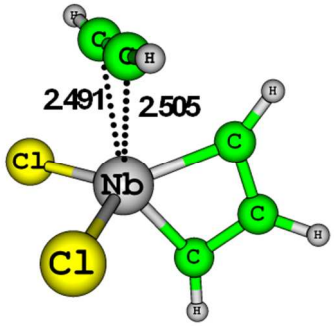
Initial van der Waals complex



E = -1171.21161240 au.

Nb	-0.068445000	-0.000188000	-0.000288000
Cl	1.236248000	1.910264000	0.000037000
Cl	1.243612000	-1.905583000	0.000041000
C	-1.543977000	-0.003057000	-1.271143000
C	-2.225001000	-0.003654000	0.000682000
C	-1.542242000	-0.003031000	1.271818000
H	-2.084562000	-0.004032000	-2.213405000
H	-3.317652000	-0.005330000	0.001125000
H	-2.081846000	-0.004049000	2.214653000

Transition state for acetylene coordination

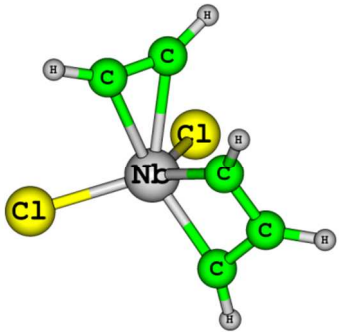


E = -1171.19117479 au

Nb	-0.044497000	-0.117554000	-0.105371000

Cl	-0.321880000	2.026221000	-1.014878000
Cl	2.037965000	-1.055715000	-0.608869000
C	1.142380000	0.375084000	2.028118000
C	0.313911000	1.282060000	1.941351000
C	-1.502354000	-1.253152000	-0.981400000
H	1.970289000	-0.272916000	2.251415000
H	-0.267297000	2.181679000	2.029585000
H	-1.916863000	-1.556072000	-1.944476000
C	-2.239857000	-1.222785000	0.224244000
C	-1.404083000	-0.828024000	1.280422000
H	-3.329645000	-1.390611000	0.296549000
H	-1.665530000	-0.760051000	2.334426000

Complex formed with acetylene

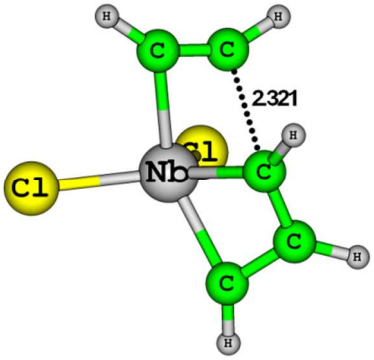


E = -1171.19244964 au

symmetry c1

Nb	-0.038269000	-0.078177000	-0.069401000
Cl	0.465441000	2.165095000	-0.535857000
Cl	-2.234848000	-0.619408000	-0.646164000
C	-0.793482000	-0.207453000	2.084890000
C	0.220349000	0.538114000	2.144859000
C	1.455712000	-1.285336000	0.786833000
H	-1.722800000	-0.617276000	2.457922000
H	0.879442000	1.254927000	2.615395000
H	1.792492000	-1.628462000	1.765241000
C	2.192853000	-1.264891000	-0.410771000
C	1.248567000	-1.060046000	-1.418840000
H	3.287992000	-1.316832000	-0.529053000
H	1.467797000	-1.086102000	-2.491506000

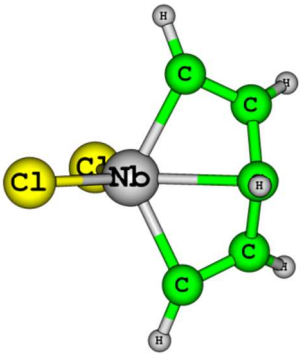
Transition state for CC bond coupling



E = -1171.19193048 au

Nb	-0.082287000	-0.075436000	-0.083771000
Cl	0.494554000	2.194949000	-0.046703000
Cl	-2.346556000	-0.377960000	-0.548000000
C	-0.511236000	-0.660963000	2.035243000
C	0.658955000	-0.162067000	2.101583000
C	1.449933000	-1.428656000	0.325024000
H	-1.431403000	-0.899311000	2.558231000
H	1.462721000	0.287095000	2.672836000
H	1.838480000	-2.095177000	1.093045000
C	2.097438000	-1.016635000	-0.871888000
C	1.070433000	-0.696642000	-1.747355000
H	3.179102000	-0.892194000	-1.041015000
H	1.215785000	-0.406590000	-2.794159000

Bicyclic product



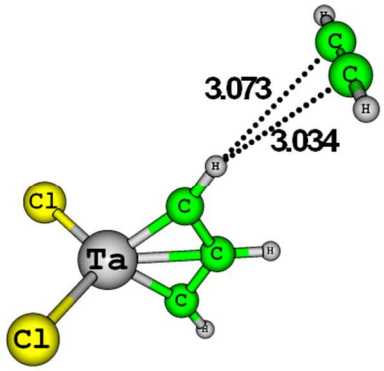
E = -1171.25661110 au

Nb	0.188672000	-0.042879000	0.000262000
Cl	-0.024928000	2.273632000	-0.001131000
Cl	2.361366000	-0.780948000	0.000000000
C	-0.607765000	-0.569507000	-1.860849000
C	-1.853773000	-0.559884000	-1.297493000
C	-1.738077000	-1.235490000	0.000590000
H	-0.322284000	-0.223240000	-2.859227000
H	-2.733642000	0.012486000	-1.627268000
H	-1.379515000	-2.261918000	0.001435000
C	-1.853456000	-0.557911000	1.297554000
C	-0.607650000	-0.567631000	1.861637000
H	-2.732416000	0.016938000	1.625443000

H -0.322804000 -0.219311000 2.859466000

1g. Structures given in Figure 5 for the mechanism using Ta complex

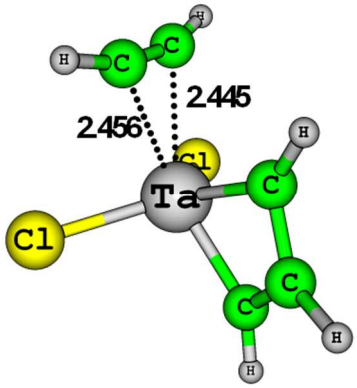
Initial van der Waals complex



E = -1171.27130834 au

Ta	-0.554327000	-0.001515000	0.098415000
Cl	-1.558111000	-1.901211000	-0.773918000
Cl	-1.547856000	1.923849000	-0.728473000
C	1.406404000	-0.008166000	0.094573000
C	1.107728000	-0.024721000	1.507166000
C	-0.236569000	-0.026723000	2.033628000
H	2.429549000	-0.006172000	-0.271103000
H	1.943603000	-0.036444000	2.211354000
H	-0.434542000	-0.040168000	3.100506000
H	5.482455000	-1.660575000	-0.557036000
C	5.429525000	-0.591452000	-0.587065000
C	5.377935000	0.615163000	-0.625397000
H	5.336086000	1.684494000	-0.664820000

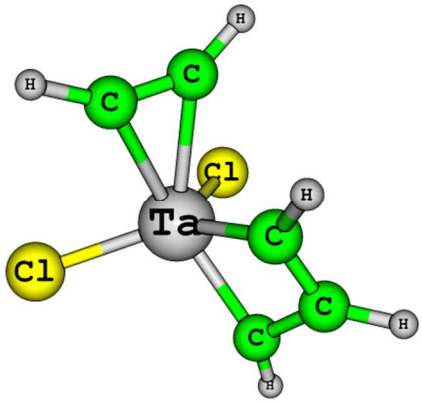
Transition state for acetylene coordination



E = -1171.25188809 au

Ta	-0.025840000	-0.075093000	-0.067955000
Cl	-0.378364000	2.065402000	-0.969070000
Cl	2.039623000	-1.020041000	-0.640803000
C	1.175153000	0.368504000	2.015409000
C	0.330168000	1.271917000	1.954863000
C	-1.487976000	-1.219148000	-0.980149000
H	2.037779000	-0.223404000	2.270366000

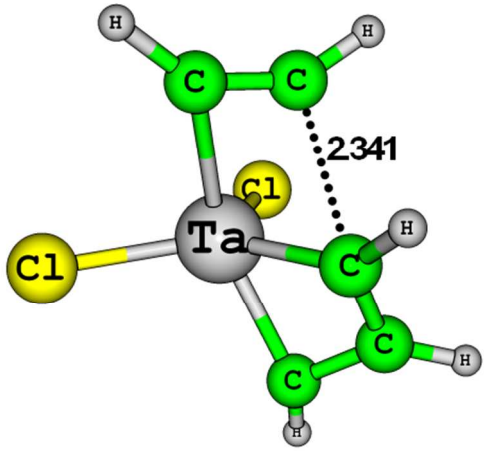
H	-0.217612000	2.184708000	2.115872000
H	-1.919804000	-1.519336000	-1.936300000
C	-2.199784000	-1.284667000	0.240834000
C	-1.376239000	-0.856206000	1.300994000
H	-3.265177000	-1.563135000	0.329664000
H	-1.638198000	-0.850610000	2.357226000



E = -1171.25319458 au

Ta	-0.030285000	-0.053008000	-0.030100000
Cl	0.414842000	2.196104000	-0.538127000
Cl	-2.186239000	-0.671133000	-0.690006000
C	-0.807216000	-0.222951000	2.093028000
C	0.190540000	0.557461000	2.165726000
C	1.505082000	-1.262588000	0.782689000
H	-1.714052000	-0.635258000	2.521927000
H	0.800857000	1.276110000	2.700294000
H	1.864657000	-1.627338000	1.745923000
C	2.234570000	-1.229495000	-0.422524000
C	1.294967000	-0.969793000	-1.427192000
H	3.325532000	-1.328430000	-0.548095000
H	1.539930000	-0.975837000	-2.494845000

Transition state of CC bond coupling

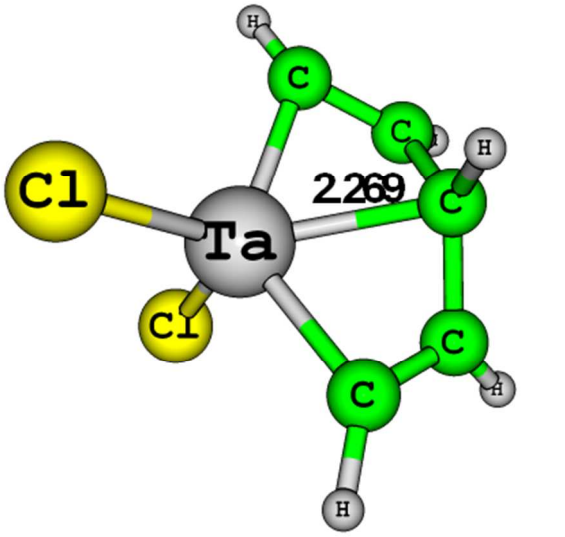


E = -1171.25264463 au

Ta	-0.066834000	-0.055895000	-0.049337000

Cl	0.481037000	2.217965000	0.119676000
Cl	-2.323554000	-0.343988000	-0.566886000
C	-0.454546000	-0.798317000	2.019035000
C	0.731706000	-0.319052000	2.092445000
C	1.485309000	-1.442565000	0.181967000
H	-1.331147000	-1.063475000	2.604811000
H	1.546544000	0.048025000	2.707762000
H	1.909947000	-2.170754000	0.871528000
C	2.107560000	-0.912495000	-0.985914000
C	1.072042000	-0.480885000	-1.807115000
H	3.187629000	-0.796126000	-1.170305000
H	1.236250000	-0.075083000	-2.812084000

Bicyclic product



E = -1171.31512892 au

Ta	0.142225000	-0.039717000	-0.000033000
Cl	0.065126000	2.286819000	0.000118000
Cl	2.288446000	-0.857518000	-0.000880000
C	-0.688242000	-0.520878000	-1.871977000
C	-1.933200000	-0.483929000	-1.300799000
C	-1.830083000	-1.160636000	0.000669000
H	-0.424966000	-0.180952000	-2.879218000
H	-2.805580000	0.096909000	-1.637111000
H	-1.530120000	-2.206137000	0.000527000
C	-1.931109000	-0.483858000	1.302082000
C	-0.685545000	-0.521608000	1.872231000
H	-2.802240000	0.098665000	1.638743000
H	-0.421155000	-0.181839000	2.879201000