Supporting Information

α,β-(C–C–C) Agostic Bonds in Transition Metal Based Olefin Metathesis Catalyses

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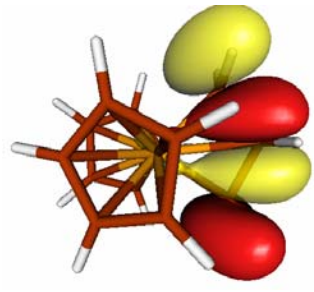
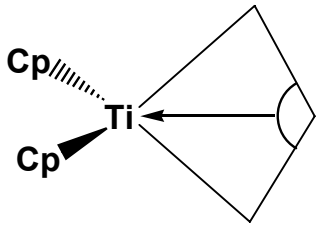
Computational Details.

All calculations were carried out using Density Functional Theory as implemented in the Jaguar 5.5 suite[1] of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP[2-5] functional and the 6-31G** basis set. The transition metals were represented using the Los Alamos LACVP** basis[6, 7] that includes relativistic effective core potentials for second and third row elements. The relative energies reported in the paper are evaluated by additional single-point calculations on optimized geometry using Dunning's correlation-consistent triple-ξ basis set[8] cc-pVTZ(-f) that includes a double set of polarization functions. For quantifying the M-C2 bond order, we made use of the Mayer bond order formalism[9-11] implemented in the Amsterdam Density Functional package (ADF)[12-14] employing the BLYP functional (note that hybrid functionals are not available in 'pure DFT' implementations, such as the ADF program) and the triple-ξ quality numerical basis set TZP that were generated from atomic calculations using the standard protocol implemented in ADF. ADF was also employed for fragment calculations in order to determine the bonding at the stationary points. We have carried out full geometry optimizations on the crystal structures of the molecules described in the following and have, in addition, studied model compounds, where some of the ligands were replaced by smaller surrogates to allow for a simpler analysis and visualization. These model compounds are labled 4a, 5a, 6a and 7a – relating them to the realistic molecules mentioned in the main text.

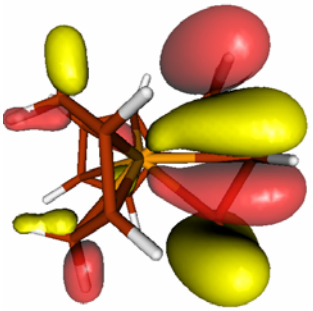
The geometries optimized from the X-ray geometries of tantalum and tungsten complexes were very large and were not characterized with frequency analysis. The rest of the geometries were characterized as minima. In some cases, a small negative frequency of value below 30 cm^{-1} observed as noise is neglected.

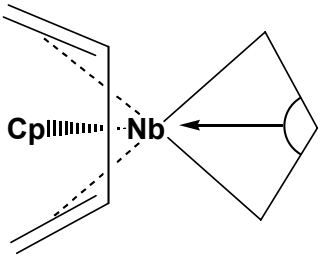
Figure 1. α,β-(C-C-C) agostic bonding MO visualized using the small molecule models. Isosurfaces are drawn for 0.025 a.u.



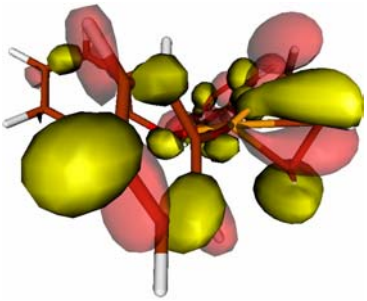


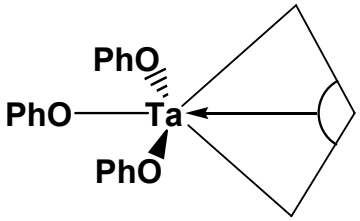
4a



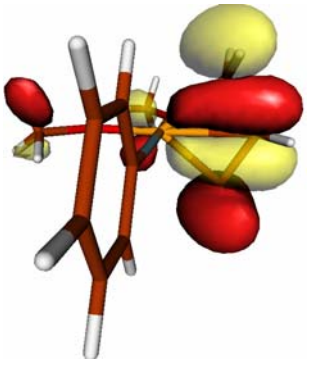


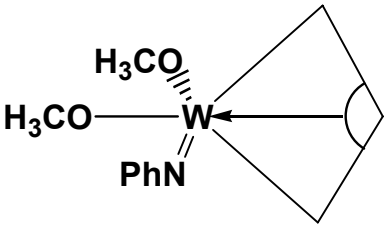
5a





6a





7a

Figure 2. Optimized structures of 16-electron ruthenium olefin complexes.

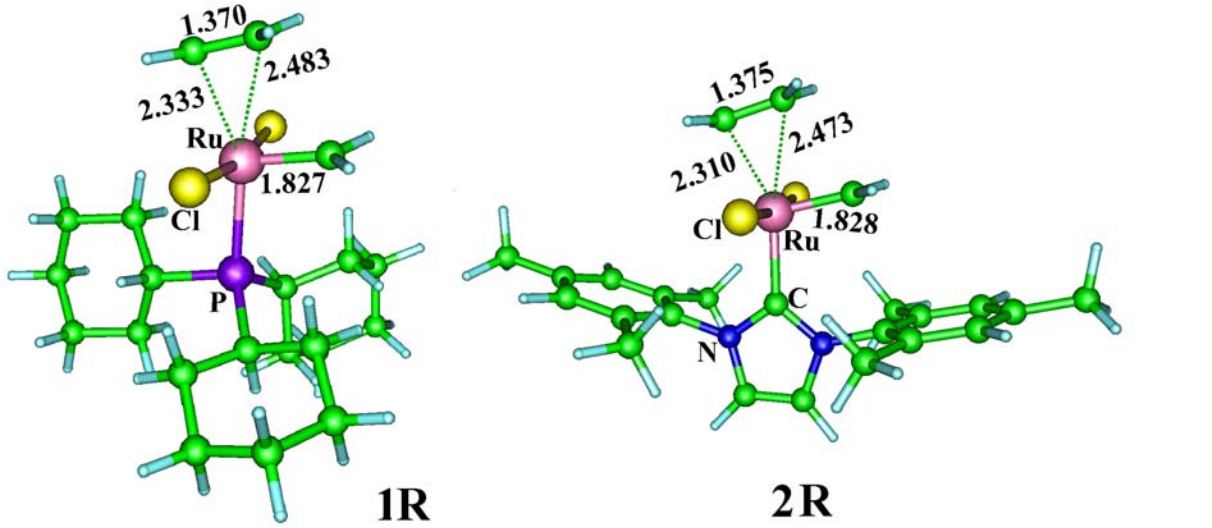


Table 1. Cartesian coordinates of optimized geometries are given below. The ID from the Cambridge Crystal Structure Database are also given.

Structure **1R**			
Ru	0.362405718	1.656287930	0.182849000
C	1.953076498	2.221103854	0.880026385
Cl	1.078726208	2.051281572	-2.125091882
Cl	-0.673913940	1.490421113	2.390819482
C	4.208025780	-0.761863247	-2.365552040
C	3.283091191	-0.400144008	-1.191083932
C	1.999050672	-1.259275616	-1.222289594
C	2.389443455	-2.755921090	-1.174299374
P	0.699215547	-0.714759379	0.032969355
C	3.295394593	-3.122714736	-2.363082922
C	4.560671172	-2.255351440	-2.390517874
C	-2.991424884	-0.784967204	-2.037754281
C	2.533148071	-1.978758908	3.628102901
C	2.151706186	-1.077865127	2.441737358
C	1.040972184	-1.723292867	1.584821978
C	-0.196440316	-2.031160867	2.457114716
C	0.191329183	-2.932191679	3.643889490
C	1.310113507	-2.313433720	4.492309644
C	-1.556751490	-0.374788908	-1.665128657
C	-0.972465157	-1.310853133	-0.584301969
C	-1.043030261	-2.780451966	-1.048030885
C	-2.486424949	-3.180895879	-1.397030932
C	-3.074843587	-2.255506110	-2.470765649
H	2.132435078	2.238900305	1.960966907
H	2.758714220	2.592570816	0.236356767
H	5.120536109	-0.156199281	-2.312233403
H	3.705294410	-0.485745316	-3.302495351
H	3.023178440	0.656088165	-1.247698275
H	3.816750730	-0.573909073	-0.245995364
H	1.501956909	-1.051437936	-2.179682370
H	1.513227399	-3.408423005	-1.163699625
H	2.940645344	-2.954685624	-0.245739949
H	3.559168678	-4.185972613	-2.307698859
H	2.735226255	-2.986511014	-3.298851377
H	5.165738262	-2.492002892	-3.273817210
H	5.178315469	-2.497648603	-1.513501661
H	-3.363409391	-0.129698627	-2.833731006
H	-3.644730160	-0.627524856	-1.168037139
H	3.305444808	-1.485675620	4.230506728
H	2.978847355	-2.910321735	3.249526790
H	3.040751246	-0.870738959	1.835223155
H	1.781347651	-0.116723747	2.815714608
H	1.420415042	-2.682070033	1.207335621
H	-0.967921600	-2.539531615	1.869603393
H	-0.627977724	-1.093465119	2.819763784
H	-0.695411130	-3.120982479	4.260509385
H	0.522964530	-3.910477278	3.264968562
H	1.592199723	-2.993569517	5.305008722
H	0.938470068	-1.392851125	4.962043458
H	-1.561141532	0.666375396	-1.316495237
H	-0.918605620	-0.379311617	-2.557035671
H	-1.599037563	-1.200540937	0.310578053
H	-0.644571964	-3.452186324	-0.279496782
H	-0.418814762	-2.909800644	-1.941110965
H	-2.507033949	-4.224113847	-1.734328385
H	-3.105399732	-3.131197454	-0.490184634

Structure **2R**			
Ru	-0.1676180430	0.8500966870	0.0774639940
C	-0.1011396030	0.9254021610	2.5295930100
C	-0.3587840340	1.0134068320	-2.3630440770
C	1.5977224380	1.3157751390	-0.0051668880
C	-4.5904326230	-1.1503462400	1.2714543780
N	-1.1925244830	-2.0336175560	0.0370841890
C	-3.2338602950	-1.4875816010	1.2910901950
C	-2.5806652690	-1.6302017090	0.0533355100
C	-3.2657048310	-1.5199339260	-1.1708419690
C	-4.6209741910	-1.1840130990	-1.1264018760
C	-0.8059036240	-3.3718905650	0.0100955270
C	-0.1039689150	-1.2126805430	0.0384362740
C	0.5447547470	-3.3872681910	-0.0073812570
N	0.9655197810	-2.0577105230	0.0112204110
C	4.3831142930	-1.2607739500	-1.2060115260
C	-5.2973446570	-0.9832762980	0.0789170580
C	-6.7600615850	-0.6083687290	0.0904469400
C	-2.5929232310	-1.7852720160	-2.4932750850
C	-2.5302072320	-1.7233478500	2.6032010790
C	3.0122112860	-1.5340932770	-1.2303128620
C	2.3633078670	-1.7088680780	0.0039724150
C	3.0499461330	-1.6571786820	1.2291236320
C	4.4200515450	-1.3847159890	1.1909403760
C	5.1017132200	-1.1761233490	-0.0108088430
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C	2.3457812800	-1.8870477640	2.5434735590
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H	-5.1106878280	-1.0368346120	2.2199196300
H	-5.1648212200	-1.0956066360	-2.0641956600
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H	4.9027883160	-1.1212646340	-2.1514844620
H	-7.2872310260	-1.0296980830	-0.7708055670
H	-6.8872803660	0.4800747520	0.0487952350
H	-7.2557721880	-0.9593103740	1.0002180810
H	-2.0546664520	-2.7391014510	-2.4888271100
H	-3.3342553170	-1.8202990250	-3.2952346530
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H	-1.9923285760	-2.6775552860	2.6050314140
H	-3.2534214550	-1.7425277660	3.4221517420
H	-1.7958292390	-0.9378918430	2.8103736840
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H	6.7463546900	0.2242255160	0.0518677880
H	7.0597955870	-1.2049893110	-0.9340787870
H	1.8000935830	-2.8367948890	2.5491426060
H	3.0666038820	-1.9076359060	3.3645907620
H	1.6163954250	-1.0937340990	2.7444282670
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H	2.9667181310	-1.5814220170	-3.3794869310
H	1.5318569780	-0.8354684580	-2.6481198280
C	-1.2960516650	2.8705886860	0.1776891340
C	-0.0048976620	3.3284268330	0.0993890160
H	-1.7833362070	2.7888987860	1.1441955690

H	-4.114521330	-2.530268938	-2.683637464
H	-2.515777755	-2.390338916	-3.407623760
C	-0.941961821	3.568643998	-0.102126213
C	0.192231438	4.119907973	0.434280690
H	-1.077256205	3.555003424	-1.179030443
H	-1.782384196	3.328609550	0.541904561
H	0.265852539	4.299423208	1.501327649
H	0.963160295	4.524186339	-0.212847123
H	-1.9013950780	2.8052463500	-0.7211449690
H	0.5374687970	3.5966546110	0.9998295960
H	0.4204628980	3.6089207020	-0.8582490410

Structure **1**

Ru	-0.211232967	2.481676309	-0.941906360
C	0.305464198	4.076030033	-1.982427522
C	-0.944117895	3.739049798	0.392246491
Cl	-2.393534338	2.548858496	-2.055399737
Cl	1.922608458	2.612376178	0.223786638
C	-0.325875362	4.726587725	-0.685172038
C	-1.197800633	0.159307270	-5.342112308
C	-0.441505600	0.516481183	-4.051223139
C	-0.834094637	-0.449664598	-2.907504761
C	-0.530683727	-1.905614549	-3.332412199
P	-0.137348774	0.061620127	-1.235318600
C	-1.295094815	-2.266298506	-4.619250008
C	-0.963215106	-1.298461017	-5.763187487
C	-3.374480540	-0.606345667	1.444716729
C	3.889097859	-1.039720408	-1.937171345
C	2.588182350	-0.221012577	-2.001624694
C	1.512189332	-0.817660190	-1.065626547
C	2.042289473	-0.901720769	0.383365833
C	3.343664259	-1.722336424	0.435582394
C	4.416712445	-1.149843374	-0.500441876
C	-2.632151559	-0.079631210	0.203936590
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C	-1.297575729	-2.226508836	0.107376986
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C	-3.427307715	-2.139875581	1.483768186
H	1.377558619	4.244967250	-2.064120939
H	-0.279313298	4.253303074	-2.882831508
H	-0.414270030	3.765101322	1.342523631
H	-2.029930734	3.785188774	0.443761607
H	0.477490407	5.262583452	-0.181215940
H	-1.155206732	5.345499505	-1.028586805
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H	-1.058662209	-3.297744764	-4.906937570
H	-2.374445469	-2.236787812	-4.415635960
H	-1.558692063	-1.541885979	-6.650801580
H	0.090667614	-1.429037097	-6.047712482
H	-4.387343283	-0.188438950	1.464943842
H	-2.866495383	-0.238962563	2.347694598
H	4.641790423	-0.580402889	-2.588373919
H	3.704319154	-2.048302313	-2.335478796
H	2.229519474	-0.193396163	-3.035796915
H	2.783802334	0.812133652	-1.694893494
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H	1.303331450	-1.366725520	1.043687429

Structure **2**

Ru	0.003914877	1.322276293	0.156011415
C	-1.356533659	2.739356189	0.349759835
Cl	-0.059279237	1.032301008	2.581921299
Cl	0.062139576	1.816035517	-2.237132894
C	1.341516604	2.747796235	0.423455305
C	-0.014423858	3.563859951	0.518178575
H	-1.948160937	2.687136138	1.261290253
H	-1.900140693	2.981499313	-0.560957289
H	1.882549771	2.699722813	1.366099852
H	1.932300077	2.996003385	-0.455760111
H	-0.042444564	3.998127223	1.517244146
H	0.006108895	4.288655859	-0.295227803
C	-4.537273805	-0.714474348	0.587921091
N	-1.044754268	-1.518470550	-0.410172313
C	-3.193330744	-1.087165243	0.695809654
C	-2.429863931	-1.102740729	-0.483806801
C	-2.978229539	-0.810684303	-1.745138819
C	-4.327415974	-0.448239621	-1.792114514
C	-0.627225013	-2.839371848	-0.583563652
C	0.024040456	-0.712306320	-0.175795128
C	0.720378913	-2.845514288	-0.457120964
N	1.110191139	-1.529001520	-0.204373720
C	4.578719657	-0.382570480	-0.908525369
C	-5.117486906	-0.381984218	-0.639973956
C	-6.562882668	0.045031940	-0.721988897
C	-2.158513847	-0.883418953	-3.008249864
C	-2.606551099	-1.469793424	2.031154329
C	3.241663573	-0.731413767	-1.124824388
C	2.487755879	-1.128462143	-0.006778152
C	3.040485317	-1.231647348	1.281700940
C	4.382889203	-0.873363590	1.436817411
C	5.162154484	-0.435910575	0.361156719
C	6.599685615	-0.025130268	0.568511693
C	2.232540945	-1.710803394	2.460593543
C	2.652294451	-0.692651157	-2.512186412
H	-5.145557847	-0.696430790	1.488774117
H	-4.770453658	-0.217867901	-2.757799964
H	-1.333483271	-3.630341189	-0.776850778
H	1.443431162	-3.642343903	-0.520971689
H	5.179510818	-0.073031913	-1.760096676
H	-7.013640952	-0.251491816	-1.673781408
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H	-7.155576305	-0.389857163	0.087997580
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H	-3.397469986	-1.558795104	2.780157464
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H	4.829151816	-0.945464666	2.425495331
H	7.057614100	-0.576363012	1.395113876

H	2.223878068	0.109738796	0.757880275
H	3.712083453	-1.751698480	1.467537076
H	3.130341015	-2.763127150	0.149840894
H	5.317887515	-1.773850775	-0.472912151
H	4.708112521	-0.152497828	-0.146283377
H	-2.593850118	1.010519024	0.220236737
H	-3.196454819	-0.342429172	-0.699610429
H	-0.672415535	-0.381641036	1.030226393
H	-0.305909650	-2.683614333	0.036031327
H	-1.862050462	-2.546119940	-0.776751788
H	-2.074276490	-3.838919826	1.327814547
H	-1.431150207	-2.486285740	2.252196872
H	-3.911524233	-2.483260078	2.405202398
H	-4.046076552	-2.501938392	0.650577338
H	6.670561059	1.042604128	0.810107036
H	7.198630684	-0.196070427	-0.330773164
H	1.723389492	-2.656736778	2.246032756
H	2.881299552	-1.866576503	3.326140259
H	1.465956495	-0.976960555	2.731400452
H	2.146278982	-1.632225095	-2.760362620
H	3.439320857	-0.529077540	-3.252716175
H	1.913464125	0.110217837	-2.611304859

$(PH_3)Cl_2Ru(C_3H_6)$ - Structure **3**

Ru	-0.015392854	0.050441813	-0.034777395
C	-0.648843226	1.817452046	0.567740849
C	-0.226548665	0.698566384	-1.879961135
Cl	2.290751584	0.794571569	0.034508172
P	0.673866822	-1.968244395	1.034877400
Cl	-2.282658234	-0.814865048	-0.014179349
C	-0.677365222	1.951420614	-1.012555222
H	-1.639633419	1.829179010	1.016834740
H	0.106354170	2.443703072	1.038078286
H	0.701099678	0.867098282	-2.423020688
H	-1.044708055	0.252453711	-2.441511056
H	-0.078643901	-3.140344683	0.836543415
H	1.995865542	-2.416397929	0.857153399
H	0.612827589	-1.839428204	2.436641628
H	-1.718208802	2.136361218	-1.276114584
H	0.019902907	2.751894546	-1.257823271

$(PH_3)_2Cl_2Ru(C_3H_6)$

Ru	0.919653716	-0.016985344	-0.039345398
C	-0.945920947	0.236589189	-1.178621785
C	-0.980890792	-0.191179845	1.055439457
Cl	1.809297503	0.359718777	-2.219544074
P	1.028460216	2.303108032	0.411513283
Cl	1.741185851	-0.479284698	2.151084910
C	-1.867416112	0.435172393	0.003258213
P	1.017024635	-2.341813708	-0.482618607
H	-0.821757869	1.070882252	-1.866491451
H	-1.107641243	-0.687036008	-1.734937967
H	-1.153504586	-1.254437052	1.224164732
H	-0.883313140	0.327348178	2.007443050
H	2.325321541	2.849004068	0.527121589
H	0.489968576	3.232129809	-0.508806660
H	0.472921483	2.819947545	1.604734512
H	-2.031298539	1.499861529	0.204187852
H	-2.854832028	-0.037580924	-0.102078271
H	2.305338658	-2.911002973	-0.571886813
H	0.439255324	-3.251183842	0.432714970
H	0.471382512	-2.847346214	-1.685003581

Calculated JEJKEO DFT Real - Structure **4**

Ti	-2.606053220	-0.184576629	-1.071945867
C	-1.377097557	0.126612552	-2.779038094
C	-0.190778669	-0.152377169	-1.813394651
C	-0.714384773	-0.966869187	-0.555516722
C	-0.080046598	-2.365268434	-0.739900715
C	1.377082264	-2.274192731	-0.224260388
C	2.030171119	-1.256191994	-1.227191794
C	0.923781715	-1.101746220	-2.358616912
C	0.221607598	-2.469756327	-2.249364358
C	1.499798108	-0.724872950	-3.717660329
C	1.531016998	-2.026090132	1.264568128
C	3.129610174	-1.583766260	2.988043827
C	3.365201231	-2.889605472	3.737668016
C	4.332746907	-0.652950848	2.973275627
C	2.449960621	0.078611065	-0.642248955
C	3.856995895	1.992137632	-1.071574229
C	5.272629230	1.850414594	-0.526120862
C	3.775921356	2.848687526	-2.328145355
O	2.833569389	-1.883675666	1.594394219
O	0.626012101	-2.043642918	2.073586731
O	3.378302364	0.663170683	-1.434215782

Calculated JEJKEO DFT Structure **4a**

Ti	-0.399835771	-0.118053194	-0.120913715
C	1.041632775	0.234432302	-1.607016180
C	2.037485319	0.220456833	-0.388023776
C	1.400734216	-0.296054541	0.955529781
H	1.254352892	-0.576079024	-2.302244878
H	1.057419648	1.181589453	-2.144232894
H	2.886405683	-0.420349973	-0.641917923
H	2.415092100	1.232353179	-0.227464691
H	1.727963433	-1.306361014	1.196207964
H	1.629830321	0.362362653	1.790045084
C	-0.871688961	-2.021491253	-1.577177116
C	-2.096636358	-1.610193132	-1.009658534
C	-2.028042724	-1.833698369	0.394158205
C	-0.757790585	-2.370594287	0.690484880
C	-0.037339188	-2.473250102	-0.527269026
H	-0.612339444	-1.969815290	-2.624063402
H	-2.937405981	-1.197175492	-1.549591025
H	-2.808820716	-1.617484734	1.109992427
H	-0.389118594	-2.625470385	1.673484314
H	0.984316829	-2.811347596	-0.631951017
C	-0.483737432	1.896448710	1.253118682

O	2.000094257	0.595034689	0.363248739
H	-1.481596563	-0.637100045	-3.549914636
H	-1.336498375	1.108771672	-3.248922644
H	0.239396171	0.799785358	-1.502152889
H	-0.369309573	-0.543299667	0.379930288
H	-0.632616431	-3.193765106	-0.291050187
H	1.875609800	-3.240151907	-0.386187011
H	2.920361731	-1.690321123	-1.689051476
H	-0.655510255	-2.519452026	-2.893752717
H	0.877904547	-3.310717301	-2.500242901
H	2.220045318	-1.476765106	-4.058744353
H	2.019498398	0.236301781	-3.675951450
H	0.706353458	-0.649128386	-4.465862545
H	2.256754583	-1.073953707	3.402653178
H	3.606008725	-2.686506118	4.785884859
H	4.197422689	-3.444845012	3.293567078
H	2.467597051	-3.511452674	3.706522044
H	4.094657912	0.256098205	2.415600485
H	5.195098245	-1.138676801	2.505529828
H	4.607146721	-0.374173807	3.995115574
H	3.192037650	2.380235598	-0.297188704
H	5.284344159	1.208327888	0.357998469
H	5.668656117	2.830936278	-0.244265097
H	5.934185630	1.414073188	-1.280757694
H	2.745800070	2.912147546	-2.688821881
H	4.396442496	2.427724945	-3.125051723
H	4.128583498	3.862588907	-2.116011839
C	-3.889929135	-1.606301564	-2.578817487
C	-4.789554569	-0.899765761	-1.746063264
C	-4.607226687	-1.362628595	-0.413628256
C	-3.575802463	-2.324427443	-0.420972611
C	-3.142557019	-2.481985752	-1.760542191
H	-3.785460119	-1.480141442	-3.646405216
H	-5.494598116	-0.147631865	-2.071186411
H	-5.140667001	-1.014219711	0.458903561
H	-3.181878254	-2.844904678	0.440690235
H	-2.368889942	-3.155256974	-2.089802710
C	-1.848412578	1.516716808	0.545168620
C	-3.168847493	1.143307051	0.894424169
C	-4.035556229	1.591813599	-0.135513199
C	-3.249941453	2.192699181	-1.141034793
C	-1.898444777	2.155539474	-0.713341664
H	-0.957135779	1.338856174	1.128235331
H	-3.461414924	0.615443829	1.792089136
H	-5.108344490	1.467400814	-0.160245531
H	-3.611724534	2.603530679	-2.073975372
H	-1.055751131	2.555666455	-1.256858902
C	-1.720942366	1.223928827	1.394817552
C	-2.381690442	1.259683083	0.139768176
C	-1.538561649	1.915176165	-0.784681188
C	-0.365552203	2.313032217	-0.092400542
H	0.239330262	2.060241507	2.037101419
H	-2.096593928	0.768287220	2.300832634
H	-3.350391936	0.832938416	-0.077899117
H	-1.742340669	2.073366151	-1.834753188
H	0.477815493	2.831657779	-0.524490088

Calculated ROMSIV01 DFT Real - Structure **5**

Nb	-1.731437046	0.247767791	-0.114738871
C	-1.503121487	-2.061987587	0.093333318
C	-0.544983805	-1.715616937	-0.913356714
C	-1.012232985	-1.031482298	-2.038682991
C	-2.418521936	-0.756629994	-2.099422517
C	-0.817991962	1.795585138	-1.368568758
C	0.350219836	1.693581243	-0.324967736
C	0.198299702	0.594364314	0.885410872
C	1.477542802	-0.145600145	0.895194143
C	1.976075269	-1.123116205	1.739585380

Calculated ROMSIV01 DFT Model - Structure **5a**

Nb	0.288210350	-0.104464939	-0.215600478
C	-0.141701239	-2.253844839	-1.033190271
C	1.072303117	-1.866705947	-1.684400844
C	1.049206913	-0.690841595	-2.441591069
C	-0.189624357	0.021746335	-2.507185945
C	1.821085144	1.391298373	-0.549142988
C	2.607765670	0.466100336	0.481938899
C	1.932477458	-0.906142598	0.946219420
C	-1.259588409	1.717478108	0.461895307
C	-2.087658086	0.660860558	-0.005608267

C	3.243659318	-1.700372910	1.452781485
C	4.006526170	-1.324526841	0.360731315
C	4.179375237	0.204970835	-1.675139846
C	3.580010398	1.204477790	-2.422687424
C	2.317442353	1.758603180	-2.076873972
C	1.671307798	1.282735407	-0.954346975
C	2.276174684	0.255528727	-0.204323749
C	3.532383642	-0.309693423	-0.518169726
H	-1.107447770	-2.420491024	1.042014800
H	-2.434109362	-2.543310849	-0.200916848
H	0.519373828	-1.839725208	-0.753445527
H	-0.305042472	-0.618231364	-2.750158801
H	-2.758997132	-0.080596857	-2.881323864
H	-3.114347918	-1.568079476	-1.895673340
H	-1.325313641	2.760566463	-1.315466963
H	-0.468137693	1.623443430	-2.383523723
H	0.440956862	2.668432433	0.168762911
H	-0.023063835	1.070974603	1.841742473
H	1.412731524	-1.464108642	2.604268665
H	3.620304551	-2.474047302	2.117234833
H	4.967695256	-1.795938012	0.174629553
H	5.146822726	-0.191518241	-1.972582649
H	4.089723059	1.583741743	-3.304475381
H	1.885113421	2.544308924	-2.690450441
C	-3.746601253	1.690369684	0.100232242
C	-4.203076700	0.350986387	0.314085349
C	-3.605036442	-0.132366309	1.517623820
C	-2.792472489	0.910661380	2.060271971
C	-2.877993617	2.037750747	1.184151805
C	-4.233463753	2.619012522	-0.976701058
C	-5.258551484	-0.365146492	-0.480254991
C	-3.929639456	-1.428514421	2.205208557
C	-2.132481596	0.882210490	3.409805749
C	-2.272736481	3.390646756	1.436165451
H	-4.468449675	2.079791466	-1.898101104
H	-3.491892868	3.382796803	-1.223698454
H	-5.145211745	3.140390231	-0.656354095
H	-5.072418612	-1.441446002	-0.531753932
H	-5.318155470	0.009318223	-1.504731025
H	-6.246364998	-0.228060945	-0.020218546
H	-4.223452064	-2.203902091	1.493333474
H	-4.760843620	-1.294436388	2.909863918
H	-3.076722195	-1.811223934	2.772158597
H	-1.295340784	1.582482957	3.475832115
H	-1.753452023	-0.113336015	3.656943544
H	-2.848792834	1.165317119	4.192486434
H	-2.110827570	3.943861956	0.507034704
H	-1.310906132	3.319897279	1.953335384
H	-2.933242756	4.000978337	2.065616038
C	-1.939223773	-0.438100970	0.880586409
C	-1.022345990	-0.062512270	1.899516759
C	-0.603001057	1.270925474	1.640606199
H	-0.080105334	-3.055242497	-0.300688269
H	-1.071045042	-2.248506104	-1.599176670
H	2.013427563	-2.372826536	-1.494053664
H	1.972836474	-0.283560614	-2.841087388
H	-0.168311240	1.022365267	-2.931973399
H	-1.102552370	-0.528106158	-2.726639086
H	1.581192358	2.361997551	-0.111265154
H	2.386646140	1.534089911	-1.467196766
H	3.527467519	0.177828460	-0.026012700
H	2.850875577	1.053494036	1.369258161
H	2.548265412	-1.757762549	0.667949123
H	1.764776132	-0.915337458	2.024816118
H	-1.145655904	2.687031288	-0.002258382
H	-2.714822591	0.688462480	-0.884127937
H	-2.436644639	-1.394093562	0.795133288
H	-0.705596779	-0.681455362	2.726787141
H	0.095952922	1.844044318	2.235516903

Calculated GIFHAE DFT Real - Structure **6**			
Ta	-0.212759880	0.672400816	0.088869778
O	-0.178670023	2.447343734	0.860599383
C	-0.557447951	3.699304106	1.252279660
C	-0.438749592	4.044093067	2.622922751
C	0.101307273	3.043145615	3.632689847
C	1.641300244	3.103260420	3.682459177
C	-0.484114427	3.199552398	5.044810265
C	-0.796082650	5.334467034	3.020610957
C	-1.261101959	6.274113664	2.103134878

Calculated GIFHAE DFT Model - Structure **6a**			
Ta	1.912329430	-0.098111910	0.045467872
O	1.841258905	1.094631135	1.543779751
C	1.299481147	1.967158557	2.426178229
C	1.617374796	1.865466222	3.786243582
C	1.058440889	2.765985564	4.692550933
C	0.187726991	3.765848112	4.251848819
C	-0.122857431	3.860632292	2.892487551
C	0.428948147	2.968141458	1.974378312

C	-1.381894958	5.914457990	0.767123588
C	-1.046018119	4.632808980	0.309040313
C	-1.251602984	4.317031300	-1.166759058
C	-2.742374858	4.415451647	-1.544595896
C	-0.410152861	5.233874030	-2.076188292
O	-2.031175968	1.037021096	-0.527652250
C	-3.379043628	0.862118974	-0.549932266
C	-4.153803174	1.180777052	0.589509310
C	-3.516683341	1.684911616	1.877279252
C	-3.514520824	0.600123377	2.972410016
C	-4.176094568	2.977037937	2.390897809
C	-5.541238652	1.006018006	0.515994883
C	-6.154912828	0.539105808	-0.641977548
C	-5.373782193	0.235774399	-1.756645878
C	-3.983549028	0.383045367	-1.738638303
C	-3.137937438	0.058165418	-2.962907141
C	-2.876129221	1.316632730	-3.812899106
C	-3.728469874	-1.065848246	-3.827783938
O	-0.371050248	-1.079277000	-0.698887697
C	-0.809250071	-2.215316931	-1.309236030
C	-1.709878947	-3.073915043	-0.638226232
C	-2.214010330	-2.799651200	0.771281496
C	-1.686408106	-3.856065650	1.762284800
C	-3.751143480	-2.727300101	0.830796599
C	-2.130940755	-4.232164011	-1.302778363
C	-1.686329723	-4.544560225	-2.583393856
C	-0.797671188	-3.685666019	-3.225791375
C	-0.343574343	-2.513527313	-2.614242162
C	0.654200385	-1.612125625	-3.328580256
C	0.314314302	-1.377295387	-4.810362246
C	2.087826829	-2.165384527	-3.193303266
C	0.891028260	-0.054798359	1.750701890
C	2.153370168	0.431778977	0.820350058
C	1.804785094	0.829577229	-0.665723732
C	1.291511052	-1.474745490	2.184989080
C	2.401669606	-1.329917788	3.259493552
C	3.624080226	-0.827398574	2.425004778
C	3.082767342	-0.808460599	0.971714647
C	2.110533046	-2.002865691	0.992060507
C	2.621282472	1.967940481	-1.325363497
C	2.017970503	2.229506562	-2.721172854
C	2.632577570	3.284844351	-0.531079140
C	4.086257943	1.505541692	-1.509425777
H	-0.189894816	2.050722162	3.278034460
H	2.074423420	2.965360604	2.688723856
H	2.046041688	2.331608446	4.347847520
H	1.971553230	4.079210261	4.055596028
H	-1.578567518	3.206901217	5.029082305
H	-0.146335722	4.120701208	5.531632842
H	-0.158674453	2.365467123	5.675534205
H	-0.710582354	5.609388002	4.066673117
H	-1.529920812	7.274344602	2.429804954
H	-1.757625278	6.640634303	0.052062338
H	-0.936725670	3.285641633	-1.341723047
H	-2.887506554	4.182697628	-2.604168929
H	-3.124737526	5.427714261	-1.373774610
H	-3.348755664	3.719730397	-0.960020720
H	-0.523760704	4.936540984	-3.124675594
H	0.652743720	5.190915578	-1.823673830
H	-0.730141904	6.278298764	-1.994449213
H	-2.477511564	1.929805614	1.653685571
H	-2.988919276	-0.301757187	2.642187892
O	0.194772246	0.587025313	-0.585798471
C	-1.101701356	0.179199533	-0.591076680
C	-1.806736003	0.017741432	0.610839822
C	-3.140466822	-0.390441876	0.582032888
C	-3.782984703	-0.631975195	-0.634413363
C	-3.078255584	-0.460030165	-1.829293155
C	-1.744185388	-0.055819762	-1.814552375
O	1.885935346	-1.405098984	-1.351274257
C	1.602899958	-2.274738590	-2.343607577
C	0.778137502	-3.379788419	-2.093617922
C	0.489861305	-4.269698159	-3.126782915
C	1.018512776	-4.070487488	-4.404892198
C	1.841825496	-2.967495783	-4.645430481
C	2.138164357	-2.067949544	-3.622243755
C	2.942983827	-1.513704654	1.250152277
C	4.217341306	-0.760951110	0.645719108
C	3.910644376	0.433168189	-0.373612347
H	2.298650730	1.085936549	4.112576795
H	1.306523049	2.685841727	5.747158191
H	-0.245142902	4.464650472	4.961048480
H	-0.800015035	4.634220027	2.541546617
H	0.192486051	3.020883450	0.917137701
H	-1.308151230	0.232172119	1.551439313
H	-3.679377299	-0.514991359	1.517235203
H	-4.821531939	-0.948210613	-0.651855937
H	-3.568910783	-0.643141684	-2.781332472
H	-1.183712082	0.077129540	-2.733901877
H	0.369166165	-3.518513576	-1.097832804
H	-0.153998764	-5.122323486	-2.930623916
H	0.789571745	-4.766609446	-5.205794493
H	2.255585146	-2.802573208	-5.636336344
H	2.772908680	-1.204307092	-3.794388214
H	2.912896665	-2.558474274	0.946554524
H	2.889839022	-1.409615979	2.331892203
H	4.816638404	-1.496415436	0.110760683
H	4.779067019	-0.337271158	1.477106965
H	4.256986672	1.394379063	0.002009149
H	4.295049060	0.228552650	-1.371181349

H	-4.536562790	0.308878707	3.240058185
H	-3.021250665	0.967655451	3.879906656
H	-4.168052598	3.755738132	1.622830132
H	-3.632601635	3.360754660	3.260571372
H	-5.215034668	2.810543614	2.695687707
H	-6.148199695	1.238712766	1.386640698
H	-7.232995422	0.411532595	-0.678744103
H	-5.855908548	-0.132784589	-2.656352840
H	-2.169539977	-0.289984984	-2.596579510
H	-2.368673226	2.085803488	-3.226482664
H	-3.816220487	1.738820902	-4.186208460
H	-2.246782475	1.076112357	-4.677951992
H	-3.933860719	-1.960983688	-3.233523622
H	-3.021591007	-1.343333209	-4.616142438
H	-4.657119964	-0.758754132	-4.321875881
H	-1.819773493	-1.828548567	1.084572866
H	-1.986629724	-3.607609432	2.786637388
H	-0.595074685	-3.926770195	1.730481277
H	-2.088814413	-4.848299717	1.529913303
H	-4.081299635	-2.464570829	1.841443669
H	-4.201349982	-3.693831667	0.579103652
H	-4.145888207	-1.979733870	0.139300671
H	-2.822928404	-4.901580587	-0.799650841
H	-2.027814006	-5.449706756	-3.076738123
H	-0.447635554	-3.929762502	-4.224086678
H	0.619760954	-0.636977574	-2.836982830
H	-0.705757327	-1.001969803	-4.932613245
H	0.410999336	-2.292042199	-5.404738275
H	1.001216542	-0.639679185	-5.239438193
H	2.812039705	-1.491681250	-3.666128650
H	2.169508772	-3.143508995	-3.680610145
H	2.374361762	-2.294146166	-2.145470625
H	0.796036587	0.610967639	2.606237826
H	2.574287404	1.320713742	1.289192148
H	1.934330441	-0.059635870	-1.287805166
H	0.446793677	-2.087667485	2.505256314
H	2.117133426	-0.637480884	4.058282443
H	2.613355572	-2.298745230	3.725785021
H	4.469517971	-1.518847135	2.503595262
H	3.980650945	0.157557188	2.743961416
H	3.865185779	-0.839605950	0.210612542
H	2.618782814	-2.948304372	1.212537505
H	1.528372939	-2.118507831	0.079991714
H	0.985141593	2.582406111	-2.645529452
H	2.018334352	1.318397923	-3.329836881
H	2.596923502	2.989236465	-3.258251705
H	3.117696816	3.172860991	0.444164898
H	1.626802253	3.667238193	-0.361028178
H	3.200103149	4.042421812	-1.083498765
H	4.579683289	1.345497670	-0.545058351
H	4.662301185	2.263604805	-2.052724545
H	4.141971149	0.570461092	-2.078007491

Calculated DFT DOWFUQ10 Real - Structure **7**				**Calculated DFT DOWFUQ10 Model -** Structure **7a**			
W	-0.020474398	-0.012001138	-0.031885763	W	0.151597530	-0.338400854	-0.487269399
Si	-0.308355684	2.624117434	-2.356441952	C	1.614137606	1.144489124	-0.646595457
Si	1.801424917	3.422955181	1.230520546	C	1.548752853	1.020239754	0.948172146
C	0.264139142	1.096039227	1.716580686	C	0.512275541	-0.040510532	1.547716500
C	0.394079598	2.254080916	0.616591927	N	-1.189479610	0.841355367	-0.541327030
C	0.608614283	1.781353400	-0.895586555	C	-2.229345665	1.735981578	-0.629090682

C	-1.472577438	1.428493009	-3.239477778
C	1.045205100	3.119407974	-3.589676910
C	-1.264522175	4.161092819	-1.815329999
C	2.107339063	4.819729748	-0.004933153
C	3.416410954	2.474832093	1.477406603
C	1.220952799	4.167362984	2.866727171
N	1.623570336	-0.664452509	0.077515546
C	2.914256178	-1.106032397	0.304626019
C	3.263656411	-1.694979582	1.555537890
C	4.595313820	-2.062513483	1.767172754
C	5.569018027	-1.878473924	0.789321950
C	5.211349762	-1.337281324	-0.442945025
C	3.897793738	-0.951279019	-0.718902808
C	3.563449691	-0.404665924	-2.103593883
C	3.873189798	-1.436888968	-3.206295556
C	4.300344161	0.916528572	-2.398073184
C	2.238675100	-1.960481632	2.651848741
C	2.101510316	-3.469597347	2.933536608
C	2.572297699	-1.198837224	3.948746829
F	-1.363749701	-4.341264873	-2.974387136
F	-0.851762271	-2.276703814	-3.453162055
F	-2.718003101	-2.728186254	-2.431981172
F	-0.667046424	-3.591457768	1.099027819
F	-1.114663391	-5.136505165	-0.373412311
F	-2.596969333	-3.617072023	0.094289398
O	-0.893723172	-1.601105648	-0.771912312
C	-0.665165759	-2.911797689	-1.172415693
C	-1.423050204	-3.071382388	-2.519559780
C	-1.280583375	-3.830064769	-0.083105249
C	0.800672629	-3.303458049	-1.389468398
F	-3.143663097	2.848088312	1.070365845
F	-3.977191724	2.318964040	-0.865427426
F	-5.109991255	1.915329438	0.950654475
F	-2.783106177	0.867587052	2.839534948
F	-2.510960575	-1.143360991	2.047103119
F	-4.516099911	-0.339610429	2.322400433
O	-1.899196130	0.662376900	0.089682338
C	-3.211248798	0.508545101	0.481166706
C	-3.870309735	1.912470205	0.420158942
C	-3.262698602	-0.025893156	1.941775915
C	-3.988041892	-0.459650274	-0.425346933
H	1.172539538	0.898129111	2.278156899
H	-0.592380181	1.282154752	2.355513737
H	-0.564867996	2.771503374	0.646725492
H	1.668960425	1.731548400	-1.144640417
H	-2.351437975	1.221410278	-2.625827811
H	-0.989756794	0.471998086	-3.465224611
H	-1.812328085	1.863999942	-4.186447019
H	1.746839653	3.848643557	-3.171086732
H	0.600620008	3.565552317	-4.486462354
H	1.624090052	2.246694356	-3.912938295
H	-2.032156234	3.930441580	-1.073309715
H	-1.772290751	4.592774420	-2.685915765
H	-0.605834447	4.931731312	-1.404626325
H	2.424963774	4.444971521	-0.982602169
H	2.904046454	5.471761944	0.371894215
H	1.219031279	5.441035201	-0.153099387
H	3.354217941	1.730316352	2.275849723
H	4.207329448	3.183330455	1.750394991
H	3.741350609	1.953905334	0.572752485
H	1.077669473	3.399945955	3.633702762
H	0.271279937	4.699978404	2.746547250
C	-2.251847663	2.711372974	-1.649148146
C	-3.300027989	3.623929481	-1.724046286
C	-4.343540970	3.583528225	-0.794413518
C	-4.330327160	2.618738624	0.217263926
C	-3.286692611	1.701702684	0.305178439
O	-0.711809339	-1.649551733	-1.607648547
C	-1.956720971	-1.598382959	-2.276915205
O	1.607235176	-1.623504378	-0.477605561
C	1.981307852	-2.861726057	-1.008547011
H	1.336689178	2.137586764	-0.988776772
H	2.574653123	0.815967718	-1.036163831
H	1.263248828	1.998005641	1.331678138
H	2.539355558	0.719122559	1.283652352
H	1.020561155	-0.853189298	2.062069102
H	-0.251540768	0.430661411	2.159953252
H	-1.439944543	2.732414427	-2.368882826
H	-3.305137253	4.369780467	-2.513930173
H	-5.160429514	4.295900084	-0.859013829
H	-5.139229413	2.580123465	0.941544456
H	-3.271176145	0.945395447	1.083320350
H	-2.391772119	-2.605210358	-2.289942349
H	-1.821617415	-1.268622947	-3.315806589
H	-2.659888123	-0.916020173	-1.784890121
H	2.149155160	-3.589809332	-0.202569782
H	2.915990074	-2.767512911	-1.578778892
H	1.194549436	-3.243917439	-1.672418024

H	1.957184991	4.885378958	3.245136535
H	4.874502892	-2.505213536	2.718871522
H	6.598558497	-2.166096015	0.981514706
H	5.969884766	-1.214681723	-1.210811492
H	2.489457700	-0.204451424	-2.131123979
H	3.363753482	-2.386993281	-3.022163460
H	4.946763050	-1.643885243	-3.270368261
H	3.549842221	-1.059314844	-4.182321441
H	4.059453517	1.688629011	-1.661506641
H	4.024601590	1.297319895	-3.387316562
H	5.386754991	0.777232099	-2.386585567
H	1.268276716	-1.606808650	2.297743278
H	1.336239892	-3.643734480	3.697167608
H	3.042361312	-3.896004226	3.297850086
H	1.807449077	-4.017228059	2.034407042
H	1.782274735	-1.349307105	4.691988289
H	2.670867432	-0.123108421	3.772323046
H	3.513398393	-1.547710669	4.387693001
H	1.252338294	-2.619195653	-2.106909711
H	0.864029703	-4.322017862	-1.776728372
H	1.352459439	-3.242741111	-0.453361590
H	-5.045596117	-0.487427030	-0.154647951
H	-3.888232689	-0.134498089	-1.460599557
H	-3.559350657	-1.455034888	-0.336965263

Table 2. X-ray geometries obtained from CCDC and the geometry parameters of the metallacyclobutane region. The four examples were chosen out of this list.

Ref.	Metal	C1-C2	C2-C3	M-C2
CUJKUN[15]	Au	1.557	1.584	2.717
XUHCOS[16]	Zr	1.559	1.572	2.588
KORFIG[17]	Ti	1.521	1.520	1.469
BUVMAG[18]	Co	1.525	1.525	2.564
DBSBFE10[19]	Fe	1.525	1.527	2.691
VETHUX[20]	Fe	1.541	1.541	2.618
SOYVUX[21]	Ir	1.539	1.532	2.715
WUWNOR[22]	W	1.521	1.528	2.762
WUWNIL[22]	W	1.541	1.526	2.730
BILWEY[23]	Ti	1.545	1.578	2.537
BILWIC[23]	Ti	1.576	1.589	2.600
DOWFUQ[24]	W	1.605	1.625	2.372
DOWFUQ10[25]	W	1.605	1.625	2.372
GAJKEH[25]	W	1.532	1.586	2.324
GIFHAE[26]	Ta	1.549	1.556	2.382
TOKZEY[27]	Ti	1.551	1.557	2.601
SESBOH[28]	Ti	1.537	1.593	2.541
TOKZEY01[29]	Ti	1.551	1.557	2.601
JEJKEO[30]	Ti	1.560	1.596	2.533
ZULIVOR[31]	Ti	1.528	1.537	2.670
DULSEI[32]	Ni	1.526	1.526	2.558
PITBOJ[33]	Cr	1.528	1.528	2.710
ZIXHAP[34]	Ti	1.538	1.547	2.646
QOFTEK[35]	Ti	1.557	1.559	2.638
QOFTAG[35]	Ti	1.552	1.553	2.614
RISHEG[36]	Ta	1.517	1.529	2.894
RISHIK[36]	Ta	1.499	1.543	2.880
FAKPAI[37]	Ta	1.473	1.592	2.781
ROMSER[38]	Nb	1.581	1.601	2.441
NAFZOJ01[39]	Ta	1.514	1.535	2.868
ROMSIV01[40]	Nb	1.562	1.652	2.403
HISKAV[40]	Ta	1.578	1.613	2.637
YIJFAY[41]	Pd	1.528	1.535	2.636
FUMJAY[42]	W	1.519	1.522	2.794
VIJREL[43]	Ru	1.532	1.544	2.774
VIJRIP[43]	Ru	1.542	1.549	2.755
YUGYUU[44]	Ru	1.551	1.551	2.814
YUGYUU01[45]	Ru	1.551	1.551	2.814
SILWUF[46]	W	1.496	1.525	2.811
KAXDES[47]	W	1.549	1.570	2.789
KAXDIW[48]	W	1.530	1.543	2.772

KAXDES10[49]	W	1.549	1.570	2.789
PCYBPT[50]	Pt	1.509	1.556	2.687
TCPPTB[50]	Pt	1.548	1.557	2.694
BPRPTB10[51]	Pt	1.626	1.626	2.755
BIBFUN[51]	Pt	1.534	1.535	2.665
CURYIX[52]	Pt	1.540	1.543	2.594
GETVOQ[53]	Pt	1.535	1.536	2.680
CPPYPT10[54]	Pt	1.832	1.475	2.709
CYPTBU[55]	Pt	1.545	1.585	2.712
CECRUX[56]	Pt	1.542	1.548	2.676
BELPAJ[57]	Pt	1.535	1.536	2.698
YEGQUW[58]	Rh	1.548	1.580	2.565
FEGXOE[59]	Rh	1.537	1.548	2.645
DIMSOH10[60]	Rh	1.531	1.541	2.739
CORMOL[61]	Rh	1.512	1.527	2.714

References

1. Jaguar 5.5, Schrödinger , Inc., Portland, Oregon, 2003.
2. Becke, A. D., *Phys. Rev. A* **1988,** *38*, 3098-3100.
3. Becke, A. D., *J. Chem. Phys.* **1993,** *98*, 5648-5652.
4. Lee, C. T.; Yang, W. T.; Parr, R. G., *Phys. Rev. B* **1988,** *37*, 785-789.
5. Vosko, S. H.; Wilk, L.; Nusair, M., *Can. J. Phys.* **1980,** *58*, 1200-1211.
6. Hay, P. J.; Wadt, W. R., *J. Chem. Phys.* **1985,** *82*, 270-283.
7. Wadt, W. R.; Hay, P. J., *J. Chem. Phys.* **1985,** *82*, 284-298.
8. Dunning, T. H., *J. Chem. Phys.* **1989,** *90*, 1007-1023.
9. Mayer, I., *Chem. Phys. Lett.* **1983,** *97*, 270-274.
10. Mayer, I., *Int. J. Quantum Chem.* **1986,** *29*, 477-483.
11. Mayer, I., *Int. J. Quantum Chem.* **1986,** *29*, 73-84.
12. Baerends, E. J.; Gritsenko, O. V., *J. Phys. Chem. A* **1997,** *101*, 5383-5403.
13. Velde, G. T.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T., *J. Comput. Chem.* **2001,** *22*, 931-967.
14. Guerra, C. F.; Snijders, J. G.; te Velde, G.; Baerends, E. J., *Theor. Chem. Acc.* **1998,** *99*, 391-403.
15. Dinger, M. B.; Henderson, W., *Journal of Organometallic Chemistry* **1999,** *577*, 219-222.
16. Binger, P.; Muller, P.; Podubrin, S.; Albus, S.; Kruger, C., *Journal of Organometallic Chemistry* **2002,** *656*, 288-298.
17. Beckhaus, R.; Flatau, S.; Trojanov, S.; Hofmann, P., *Chemische Berichte-Recueil* **1992,** *125*, 291-299.
18. Hughes, R. P.; Samkoff, D. E.; Davis, R. E.; Laird, B. B., *Organometallics* **1983,** *2*, 195-197.
19. Flippen, J. L., *Inorganic Chemisty* **1974,** *13*, 1054.
20. Karel, K. J.; Tulip, T. H.; Ittel, S. D., *Organometallics* **1990,** *9*, 1276-1282.
21. Tjaden, E. B.; Schwiebert, K. E.; Stryker, J. M., *Journal of the American Chemical Society* **1992,** *114*, 1100-1102.
22. Tsang, W. C. P.; Hultzsch, K. C.; Alexander, J. B.; Bonitatebus, P. J.; Schrock, R. R.; Hoveyda, A. H., *Journal of the American Chemical Society* **2003,** *125*, 2652-2666.
23. Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H., *Journal of the American Chemical Society* **1981,** *103*, 7358-7361.
24. Schaverien, C. J.; Dewan, J. C.; Schrock, R. R., *Journal of the American Chemical Society* **1986,** *108*, 2771-2773.
25. Schrock, R. R.; Depue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H., *Journal of the American Chemical Society* **1988,** *110*, 1423-1435.
26. Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R., *Journal of the American Chemical Society* **1988,** *110*, 4964-4977.
27. Polse, J. L.; Andersen, R. A.; Bergman, R. G., *Journal of the American Chemical Society* **1996,** *118*, 8737-8738.
28. Tomaszewski, R.; Hyla-Kryspin, I.; Mayne, C. L.; Arif, A. M.; Gleiter, R.; Ernst, R. D., *Journal of the American Chemical Society* **1998,** *120*, 2959-2960.
29. Polse, J. L.; Kaplan, A. W.; Andersen, R. A.; Bergman, R. G., *Journal of the American Chemical Society* **1998,** *120*, 6316-6328.

30. Stille, J. R.; Santarsiero, B. D.; Grubbs, R. H., *Journal of Organic Chemistry* **1990,** *55*, 843-862.
31. Rosenthal, U.; Lefeber, C.; Arndt, P.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V., *Journal of Organometallic Chemistry* **1995,** *503*, 221-223.
32. Hughes, R. P.; Carl, R. T.; Samkoff, D. E.; Davis, R. E.; Holland, K. D., *Organometallics* **1986,** *5*, 1053-1055.
33. Hao, S. K.; Song, J. I.; Berno, P.; Gambarotta, S., *Organometallics* **1994,** *13*, 1326-1335.
34. Brinkmann, P. H. P.; Prosenc, M. H.; Luinstra, G. A., *Organometallics* **1995,** *14*, 5481-5482.
35. Greidanus, G.; McDonald, R.; Stryker, J. M., *Organometallics* **2001,** *20*, 2492-2504.
36. Rietveld, M. H. P.; Hagen, H.; vandeWater, L.; Grove, D. M.; Kooijman, H.; Veldman, N.; Spek, A. L.; vanKoten, G., *Organometallics* **1997,** *16*, 168-177.
37. Wallace, K. C.; Dewan, J. C.; Schrock, R. R., *Organometallics* **1986,** *5*, 2162-2164.
38. Mashima, K.; Kaidzu, M.; Nakayama, Y.; Nakamura, A., *Organometallics* **1997,** *16*, 1345-1348.
39. Rietveld, M. H. P.; Teunissen, W.; Hagen, H.; vandeWater, L.; Grove, D. M.; vanderSchaaf, P. A.; Muhlebach, A.; Kooijman, H.; Smeets, W. J. J.; Veldman, N.; Spek, A. L.; vanKoten, G., *Organometallics* **1997,** *16*, 1674-1684.
40. Mashima, K.; Kaidzu, M.; Tanaka, Y.; Nakayama, Y.; Nakamura, A.; Hamilton, J. G.; Rooney, J. J., *Organometallics* **1998,** *17*, 4183-4195.
41. Hoffmann, H. M. R.; Otte, A. R.; Wilde, A.; Menzer, S.; Williams, D. J., *Angewandte Chemie-International Edition in English* **1995,** *34*, 100-102.
42. Hein, J.; Jeffery, J. C.; Marken, F.; Stone, F. G. A., *Polyhedron* **1987,** *6*, 2067-2071.
43. Diversi, P.; Ingrosso, G.; Lucherini, A.; Marchetti, F.; Adovasio, V.; Nardelli, M., *Journal of the Chemical Society-Dalton Transactions* **1991**, 203-213.
44. McNeill, K.; Andersen, R. A.; Bergman, R. G., *Journal of the American Chemical Society* **1995,** *117*, 3625-3626.
45. McNeill, K.; Andersen, R. A.; Bergman, R. G., *Journal of the American Chemical Society* **1997,** *119*, 11244-11254.
46. Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; Oregan, M. B.; Thomas, J. K.; Davis, W. M., *Journal of the American Chemical Society* **1990,** *112*, 8378-8387.
47. Feldman, J.; Davis, W. M.; Schrock, R. R., *Organometallics* **1989,** *8*, 2266-2268.
48. Feldman, J.; Murdzek, J. S.; Davis, W. M.; Schrock, R. R., *Organometallics* **1989,** *8*, 2260-2265.
49. Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R., *Organometallics* **1990,** *9*, 2535-2548.
50. Rajaram, J.; Ibers, J. A., *Journal of the American Chemical Society* **1978,** *100*, 829-838.
51. Klingler, R. J.; Huffman, J. C.; Kochi, J. K., *Journal of the American Chemical Society* **1982,** *104*, 2147-2157.
52. Parsons, E. J.; Larsen, R. D.; Jennings, P. W., *Journal of the American Chemical Society* **1985,** *107*, 1793-1794.
53. Neilsen, W. D.; Larsen, R. D.; Jennings, P. W., *Journal of the American Chemical Society* **1988,** *110*, 3307-3308.

54. Gillard, R. D.; Keeton, M.; Mason, R.; Pilbrow, M. F.; Russell, D. R., *J. Organomet. Chem.* **1971,** *33*, 247.
55. Yarrow, D. J.; Ibers, J. A.; Lenarda, M. L.; Graziani, M., *J. Organomet. Chem.* **1974,** *70*, 133.
56. Burton, J. T.; Puddephatt, R. J.; Jones, N. L.; Ibers, J. A., *Organometallics* **1983,** *2*, 1487-1494.
57. Ibers, J. A.; Dicosimo, R.; Whitesides, G. M., *Organometallics* **1982,** *1*, 13-20.
58. Vogt, M.; Reggelin, M.; Schollmeyer, D., *CCDC 166888* **2001**.
59. Wick, D. D.; Northcutt, T. O.; Lachicotte, R. J.; Jones, W. D., *Organometallics* **1998,** *17*, 4484-4492.
60. Andreucci, L.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Marchetti, F.; Adovasio, V.; Nardelli, M., *Journal of the Chemical Society-Dalton Transactions* **1986**, 477-487.
61. Periana, R. A.; Bergman, R. G., *Journal of the American Chemical Society* **1984,** *106*, 7272-7273.