

APPENDIX (supplementary data for deposition): Listing of calculated atomic coordinates for the $[\text{OB}_{11}\text{H}_{12}]^-$ anion **2**, $[(\eta^6\text{-C}_6\text{H}_6)\text{FeOB}_8\text{H}_{10}]$ **5A**, $[(\text{PMe}_2\text{Ph})_2\text{PtOB}_8\text{H}_{10}]$ **6/6A**, $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuOB}_9\text{H}_{13}]$ **7/7A**, $[(\eta^6\text{-C}_6\text{H}_6)\text{RuB}_9\text{H}_{13}]$ **8A**, and for $[4\text{-}(\eta^6\text{-C}_6\text{H}_6)\text{-}n\text{-}arachno\text{-}4\text{-RuB}_8\text{H}_{14}]$ **19A**.

Calculated coordinates (DFT; B3LYP / 6-31G*) for the $[\text{OB}_{11}\text{H}_{12}]^-$ anion (species 2).

O 1.6760902303 0.4804728318 0.1580617702
B -0.8233390189 -0.5434010001 1.2914623747
B -0.6340430621 1.1777526275 1.3886201574
B 0.9302379159 -0.2242836055 1.2843490251
B 0.2142839408 -1.6484704412 0.3500393324
B -1.7769068386 0.5597127034 0.2262197254
B -0.8527504491 0.4181648653 -1.3186955057
B 0.19524108 -1.0259198027 -1.3398719803
B 0.9029142031 0.6692155714 -1.141074743
B -1.2787713061 -1.0547276406 -0.3741400208
B -0.6528262641 1.7924241213 -0.2799045703
B 1.6620067666 -0.9216974314 -0.3582779477
H -1.3219991383 0.7078563628 -2.381150221
H 0.2542671375 -1.7046106439 -2.3233094981
H 1.5600245437 1.2116173107 -1.9782422269
H -2.1731946558 -1.8026932388 -0.6396058049
H -0.8837307876 2.9096923706 -0.6334970376
H 2.7049074566 -1.4647311534 -0.5700914011
H -2.9560953623 0.7432470045 0.307110775
H 0.2002705963 1.9328046277 0.709789838
H 0.287834283 -2.8024760754 0.6568231087
H -1.2692878982 -1.0155521188 2.2970110969
H -0.8497140732 1.7969864455 2.3869526751
H 1.6077612178 -0.3497733836 2.2600852981

Calculated coordinates (DFT; B3LYP / 6-31G*) for $[(\eta^6\text{-C}_6\text{H}_6)\text{FeOB}_8\text{H}_{10}]$ (compound 5A).

Fe 0.5709327691 -0.0795137636 0.0020911246
B -0.9238139594 -0.8937422547 1.1977622213
B -1.0983961092 0.8527563679 0.9332220458
B -2.5999357236 0.0502843164 1.3789204165
B -0.8996748169 -0.7655652101 -1.2991761029
B -2.6246877529 1.2154601857 0.0372391233
B -1.0803399206 0.9451590004 -0.8605678256
B -3.6228182499 -0.1837819827 -0.0447135209
B -2.5719267561 0.193992244 -1.4162583009
H 2.2768347029 -1.128379501 2.1762851166
H 1.8707432148 1.3381478318 2.1988128293
C 2.2796772634 -0.568429862 1.2483688349
H 2.4667118151 -2.3268506299 -0.0020002805
C 2.0573275214 0.8281881285 1.2609704765
H -0.647106735 -1.5460792429 2.1572913836
C 2.4040548352 -1.2439531537 0.012559792
C 1.96676781 1.5425186871 0.0432159715
H -0.7885877403 1.6495273255 1.7684792825
H -3.0853867529 0.1649785792 2.4581376983
H 1.7036989273 2.5936761716 0.0536378688
C 2.315828898 -0.5344036515 -1.2076152812
O -0.7478056243 -1.5373609809 -0.0853916786
H 2.3371611695 -1.0701051916 -2.1496150015
C 2.0939238679 0.8613532749 -1.1909416142
H -3.1141887667 -1.043870444 0.8776954744
H 1.9365248047 1.3969389689 -2.1197802584
H -3.1281341318 2.2926838383 0.0878576015

H -4.8014654913 -0.3202547172 -0.0634817722
H -0.6015981071 -1.3157400997 -2.3148415511
H -0.7535217652 1.8227409999 -1.6033803097
H -3.095175502 -0.9451356639 -1.0403991157
H -3.035831377 0.4195136017 -2.4874241365

Calculated coordinates (DFT; B3LYP / 6-31G*) for [(PMe₂Ph)₂PtOB₈H₁₀] (compound 6/6A).

Pt 0.2247252357 0.0470633416 0.6120483742
B 0.2258544771 0.0386316832 2.8620839777
B 1.8719141867 0.0359279309 2.1259727091
B 1.9510364226 -1.3543336856 0.9802972891
P -1.7209051652 1.4091217622 0.5040214768
P 0.51273562 -0.3749766101 -1.7281859669
B 0.1530958078 -1.5774814639 3.7666499944
B 2.7335379232 -1.4260100542 2.5969432675
B 1.6661715386 -0.5632635337 3.7661646897
B 1.7020636435 -2.8321288238 2.0656114308
C -2.4865423874 2.0072071563 2.0784309481
C -1.4204321371 3.0183129558 -0.3605271339
H -0.3253185608 0.9140340797 3.4513557134
H 2.4852232248 1.0476171361 1.9448231965
C -3.1767592103 0.6589774978 -0.3454927956
H -0.6064930598 -0.9575527565 2.8229707582
C 2.0653093146 0.3362834061 -2.4205664287
H 2.721577405 -1.5556601297 0.0926920501
H 1.0982607344 -2.3329815856 0.9537544186
C -0.7514821731 0.1825353809 -2.9681243444
C 0.6013698279 -2.1768569902 -2.1425362614
B 1.8650927825 -2.3022640498 3.8443774288
H -1.7579718095 2.5990524139 2.6385594676

H -3.3706847565 2.6160013506 1.8612177068
H -0.5862851857 3.514317418 0.1453176186
H -2.2916715852 3.6805413133 -0.329078828
H -2.7784676257 1.1547515583 2.6962829086
H 2.0659399628 0.0657721388 4.6950409121
H -1.1335960776 2.8492382557 -1.4011141225
C 2.8576383733 1.1758808948 -1.6252583176
C -4.1767716387 1.4244020131 -0.9649120942
H -0.5627289223 -1.7575368888 4.7004004052
H 3.9226311889 -1.4362328749 2.6611445538
C -3.3083518351 -0.7390636098 -0.3295423766
H -0.8278234471 1.2731496115 -2.9658445258
C 2.465590476 0.0743949322 -3.7414543938
O 0.6144937103 -2.8519131771 3.10665521
H -1.7285409465 -0.2358864063 -2.7118267656
H -0.4773071616 -0.1412811938 -3.9775407923
H 2.1000546678 -3.914507827 1.7707984726
H 1.4253851522 -2.6375771557 -1.5940849516
H 0.7459078002 -2.3366111755 -3.2161002839
H -0.3350258178 -2.6546062309 -1.8366437584
C 4.0246019878 1.7448179182 -2.1408629301
H -4.1027930328 2.5079783019 -0.9918241291
H 2.5643071209 1.3690183542 -0.5977214323
C -5.2793979427 0.8061400456 -1.5571885997
H 2.313676092 -2.9505188564 4.7311692278
C 3.6327831126 0.6395976605 -4.2537778883
H -2.5314643651 -1.3393588978 0.138451996
C -4.4161725724 -1.3568101203 -0.913330993
H 1.871463738 -0.5758781093 -4.3787315483
H 4.6309934729 2.3895565026 -1.5108334086
C 4.4139171411 1.4777829185 -3.4535264895

H -6.0428408394 1.4117358661 -2.038208651
H 3.9334031032 0.4244210516 -5.2757336861
C -5.4022238467 -0.5847997202 -1.5309845756
H -4.5060783352 -2.4394287853 -0.8881053144
H 5.3242037968 1.9166216371 -3.8531616175
H -6.2622036654 -1.0642046737 -1.990548997

Calculated coordinates (DFT; B3LYP / 6-31G*) for $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuOB}_9\text{H}_{13}]$ (compound 7/7A).

B 1.8718046826 -0.01529116 1.2208056814
Ru 0.0864610783 -0.001459513 -0.1130736646
B 1.7173651466 -1.5569301913 0.3270748119
B 1.725200387 1.5385791527 0.3500793538
B 3.3356801974 0.8972825363 0.8635136963
B 3.3297298032 -0.9332210934 0.8519363923
H 1.6583463949 -0.0179282055 2.3989403838
B 1.5434886328 1.335278807 -1.4596797315
B 1.5351251535 -1.3256378677 -1.4789540795
B 3.0803006761 -1.8721745241 -0.7245033457
B 3.0880349622 1.8638005557 -0.6957844857
C -2.0136712497 0.7234558464 -0.9022878304
C -1.9916739426 -0.717514475 -0.9050915739
H 4.0093046714 -1.0417034945 -0.2805444565
H 4.0130230382 1.0200467866 -0.2699003561
C -1.7115430598 1.4419392356 0.2873245894
C -1.7483931976 -1.432653477 0.3002918302
H 1.2781195816 2.5105314069 0.8828210332
H 1.2645190914 -2.5349811466 0.8449058492
H 3.9464606517 1.4855323098 1.6992727822
C -1.3822277629 0.7226664079 1.4907615284
C -1.3790212098 -0.7116355541 1.4894494583

H 3.9360327991 -1.5356784126 1.6807643528
O 1.2291857439 0.0086580332 -1.9215615474
H 1.0334286786 -2.1745719108 -2.1536174311
H 1.043199414 2.1964688707 -2.1204822771
H 3.0866857508 -1.3788579899 -1.8635858917
H 3.0839859971 1.3892693539 -1.8442921636
H 3.4651887272 2.9915864285 -0.7320167142
H 3.4487083749 -3.0024001901 -0.7752325735
C -1.8601665016 -2.9410239188 0.3519473928
C -2.2540887775 -1.4593279796 -2.1994310264
C -2.3786427472 1.4502044839 -2.1812623602
C -1.7268044979 2.9550620891 0.29735233
C -1.1131719656 1.5029086924 2.7602615643
C -1.0555361858 -1.4790816172 2.752603527
H -2.4304224383 -3.248709297 1.2341723714
H -0.873181897 -3.4132694364 0.4119220295
H -2.3744177216 -3.3410826093 -0.5217412286
H -1.6902043058 -2.3917541606 -2.2461460127
H -1.9573039977 -0.8657924071 -3.0648734421
H -3.3208503895 -1.6991914989 -2.3088983718
H -2.6253590957 2.4956798643 -1.9994753871
H -3.2522365533 0.9861224695 -2.6498527519
H -1.5583980844 1.4221380008 -2.9078583545
H -1.1235883105 3.3571616767 1.109798446
H -2.752517754 3.3296592549 0.4202936271
H -1.3243078465 3.3674273515 -0.6292442515
H -1.0379886436 0.8559581492 3.6324785526
H -1.9303617736 2.2088758606 2.9457993844
H -0.182573115 2.0744962149 2.6851759358
H -0.2495254626 -1.0040243472 3.3120233389
H -0.7269607846 -2.4933100037 2.5297511587

H -1.9385800116 -1.5411740574 3.4034179977

Calculated coordinates (DFT; B3LYP / 6-31G*) for $[(\eta^6\text{-C}_6\text{H}_6)\text{RuB}_9\text{H}_{13}]$ (compound 8A).

B -1.4042279471 -0.0271771993 1.2966078627

B -0.8208015985 -1.316005117 -1.2586840252

B -0.8312257144 1.3557924641 -1.2110671899

B -2.433052247 1.8290917482 -0.7164150157

B -2.4184714768 -1.8199964954 -0.7809566096

B -1.1980773783 1.5704083847 0.4930696159

B -1.1854813488 -1.5934202849 0.4368559916

B -2.8321672442 -0.9478045648 0.7925371006

B -2.8395651172 0.8991114725 0.8250236246

H -0.324529984 2.0600697008 -2.0318637123

H -0.3086450337 -1.9870058947 -2.1038122699

H 2.4401066352 -1.1266440808 -2.0657222972

H 2.4286892201 1.3714745362 -1.9284215866

H -2.0877933665 1.1127841511 -1.7546698516

H -2.0806611622 -1.0650479441 -1.7936053179

C 2.3627711642 -0.6328474426 -1.1035838424

C 2.3577440373 0.7750320207 -1.0257493705

H -2.9298862699 -2.821932582 -1.1668858761

H -2.9543110459 2.8382968248 -1.0689026916

H -3.4026162757 0.9978648451 -0.3592993951

H -3.3950113748 -1.0102843946 -0.3942901223

H 2.1700847039 -2.4852018354 0.0144531463

Ru 0.3179319477 0.0030796018 -0.0680091532

C 2.2147655573 -1.4035966822 0.0776535846

H 2.145620893 2.4928965406 0.285616229

C 2.2019755555 1.4113455327 0.2312872486

H -0.7538233653 -2.5349046444 1.0329508075

H -0.7742314548 2.4932735057 1.1227623201
H -3.5616838968 -1.5368448134 1.525621546
C 2.110484269 -0.7671212402 1.339921842
C 2.1016723167 0.6401834744 1.4170894625
H -3.5745261222 1.455837904 1.5776362785
H 1.984081656 -1.3627224375 2.2373505077
H 1.9700275499 1.1327673882 2.3742080777
H -1.2610240423 -0.0481552646 2.4847066232

**Calculated coordinates (DFT; B3LYP / 6-31G*) for [4-(η^6 -C₆H₆)-*n*-arachno-4-RuB₈H₁₄]
(compound 19A).**

Ru -0.4309523884 0.0899533275 -0.1592801416
B 2.9015254861 -1.2192612339 -1.048637927
B 2.8002552525 0.8006824074 0.9942078154
B 0.9873908001 1.5393574511 0.6661980968
B 3.8019634027 0.1187252569 -0.3189164936
B 1.331873051 -0.1305661833 1.1215347998
B 0.6316013951 1.8692181909 -1.2178475289
B 2.8726951947 -0.952540903 0.6718766817
B 1.3080702534 -1.3494901094 -0.1890578493
H 3.4053205205 1.3499275639 1.8576230703
H 0.6093033044 2.3033709343 1.5021478654
H 4.9794972248 0.2228808811 -0.4214458596
H 3.4576474645 -2.0850541929 -1.6404191283
H 1.6738984925 -1.0773305831 -1.4624560071
H 1.4659976395 2.2870224794 -0.2593843035
H 3.2957487649 -0.0515098843 -1.5594356045
H 3.2676900654 1.3096261594 -0.1571550753
H 1.0233759593 -0.3538057637 2.2570647426
H 3.3830105236 -1.7234122514 1.4200660812

H 0.3227964934 0.5696353331 -1.5779709824
H -0.192803246 2.724055568 -1.363430069
H 1.5092366915 1.8706192545 -2.0539618861
H -1.816383205 0.335506561 2.5597560012
H -2.5751856997 2.0777851549 0.9190281208
C -2.0175943084 0.0630504657 1.5296129639
C -2.4438220958 1.0494163109 0.6010728086
C -2.619470993 0.6969462406 -0.7529287808
C -2.4314629516 -0.6511894984 -1.1828246492
C -2.0476580739 -1.6364295294 -0.2554055053
C -1.8105680405 -1.2705536129 1.0998747826
H -1.8714863223 -2.655800874 -0.5793594173
H -2.5626864596 -0.907009384 -2.2284203882
H -2.8738566526 1.4608444804 -1.479456902
H -1.4506688547 -2.0134367241 1.802854584
H 0.9580369854 -2.4899277656 -0.1605163042