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Supplementary Materials

Mechanistic Investigations of CO-Photoextrusion and Oxidative Addition Reactions of Early Transition-Metal Carbonyls: $(\eta^5\text{-}C_5H_5)M(CO)_4$ (M = V, Nb, Ta)

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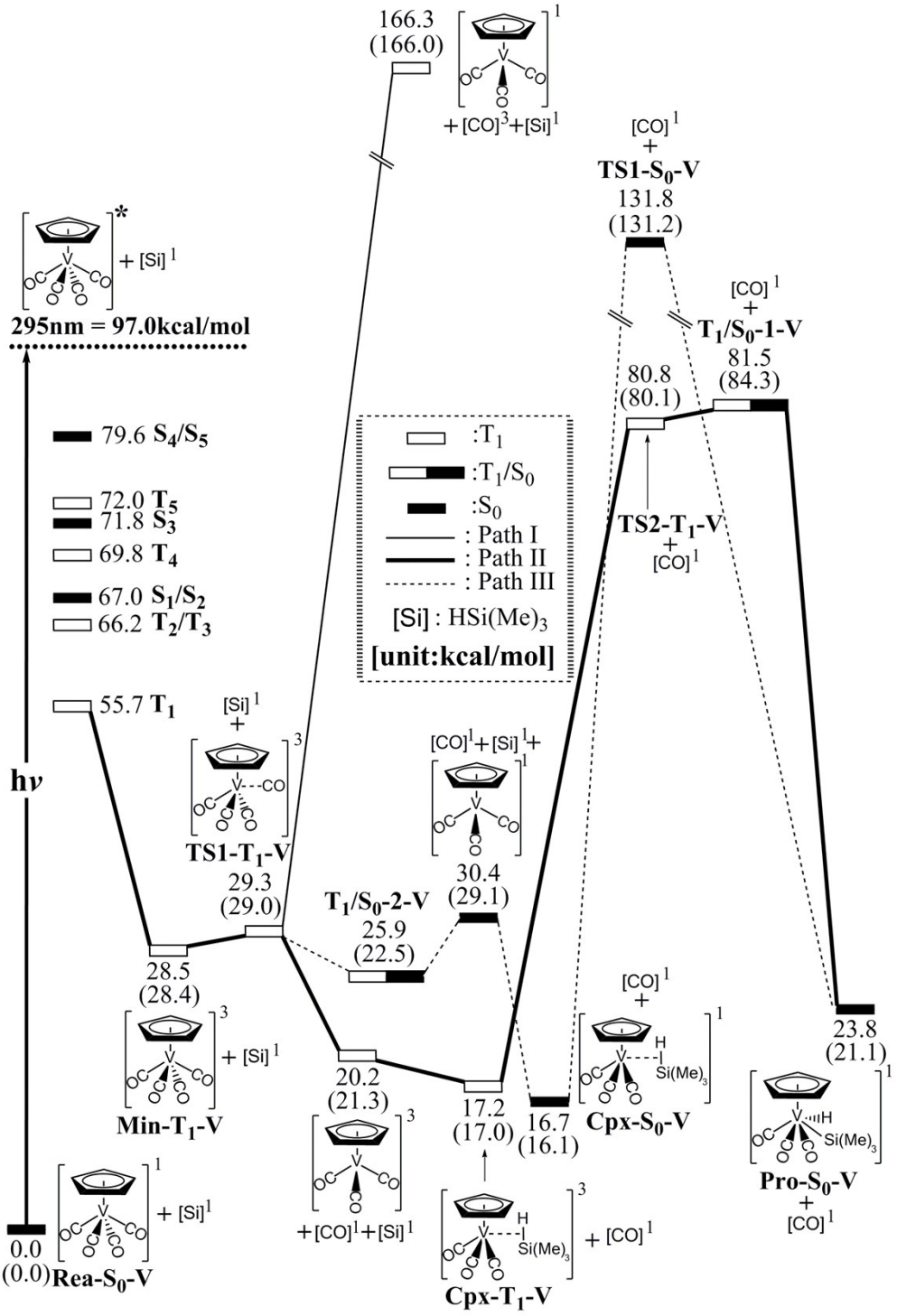

Figure S1 The energy profiles for the photochemical oxidative addition of a $(Me)_3Si–H$ bond to η^5-$CpV(CO)_4$ (**Rea-S0-V**). The relative energies are obtained at the M06-2X/Def2-SVPD level of theory. All energies (in kcal/mol) are given with respect to the reactant (**Rea-S0-V**). The solvent effect (SCRF = PCM, solvent = heptane) have been considered using the For the M06-2X/Def2-SVPD + PCM(solvent)= heptane)//M06-2X/Def2-SVPD method, whose computational values are given in the parenthesis. For more information, see IV Conclusion.

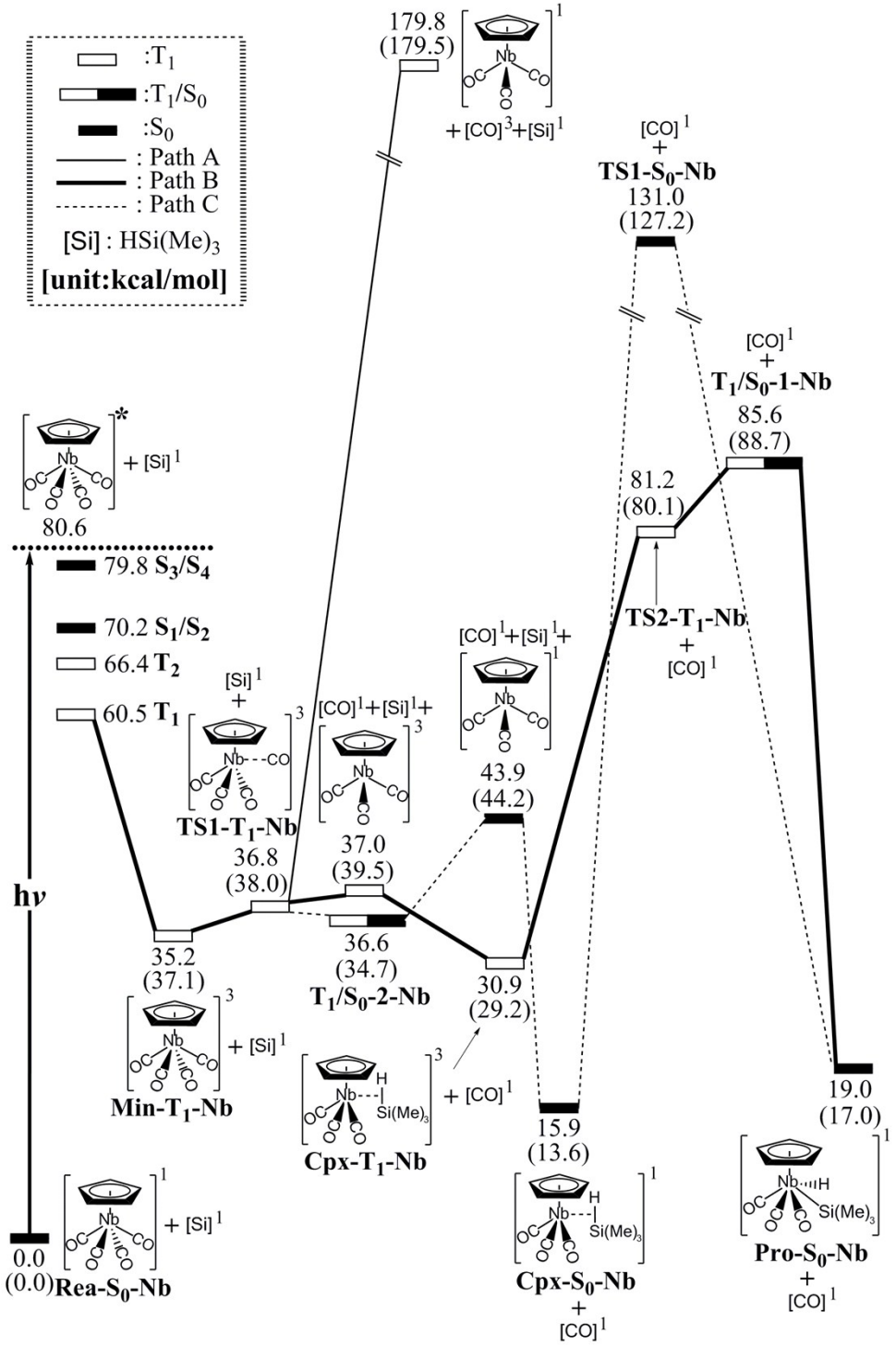

Figure S2 The energy profiles for the photochemical oxidative addition of a $(Me)_3Si–H$ bond to η^5-$CpNb(CO)_4$ (**Rea-S$_0$-Nb**). The relative energies are obtained at the M06-2X/Def2-SVPD level of theory. All energies (in kcal/mol) are given with respect to the reactant (**Rea-S$_0$-Nb**). The solvent effect (SCRF = PCM, solvent = heptane) have been considered using the For the M06-2X/Def2-SVPD + PCM(solvent)= heptane)//M06-2X/Def2-SVPD method, whose computational values are given in the parenthesis. For more information, see IV Conclusion.

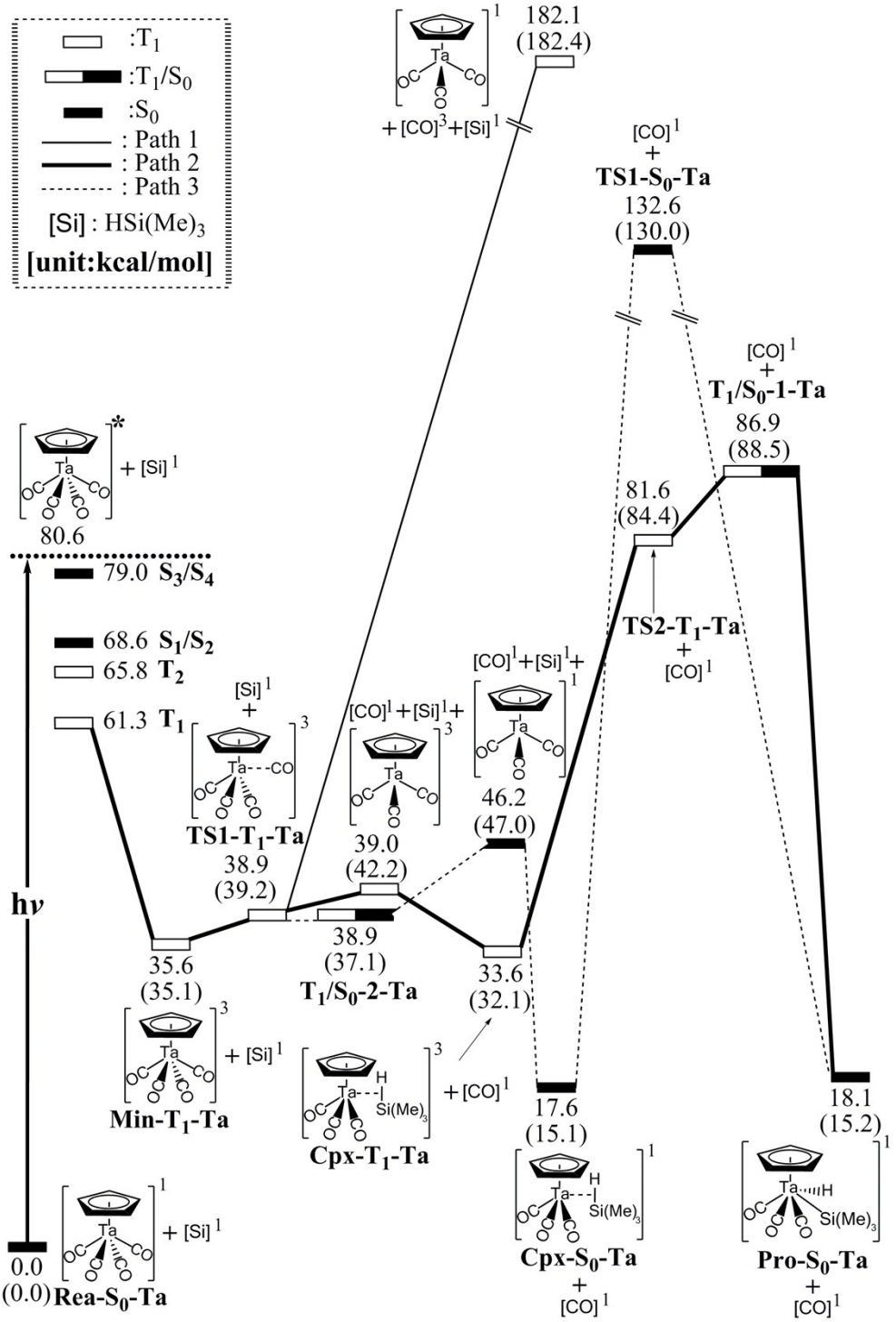

Figure S3 The energy profiles for the photochemical oxidative addition of a $(Me)_3Si–H$ bond to η^5-$CpTa(CO)_4$ (**Rea-S$_0$-Ta**). The relative energies are obtained at the M06-2X/Def2-SVPD level of theory. All energies (in kcal/mol) are given with respect to the reactant (**Rea-S$_0$-Ta**). The solvent effect (SCRF = PCM, solvent = heptane) have been considered using the For the M06-2X/Def2-SVPD + PCM(solvent)= heptane)//M06-2X/Def2-SVPD method, whose computational values are given in the parenthesis. For more information, see IV Conclusion.

Table S1. The vertical excitation energies and oscillator strengths for the fifteen lowest energy triplet excited states of molecules (η^5-CpV(CO)$_4$ (**Rea-S$_0$-V**), (η^5-CpNb(CO)$_4$ (**Rea-S$_0$-Nb**), and (η^5-CpTa(CO)$_4$ (**Rea-S$_0$-Ta**),) at the TD-DFT/M06-2X/Def2-SVPD.

TDDFT-Rea-S$_0$-V

Excited State	1:	Singlet-?Sym	2.9018 eV	427.26 nm	f=0.0150	<S**2>=0.000
56 -> 59	-0.23250					
56 -> 75	-0.14486					
57 -> 58	0.38483					
57 -> 59	-0.12820					
57 -> 62	0.17992					
57 -> 67	-0.12658					
57 -> 72	0.12998					
57 -> 74	-0.36785					
57 -> 75	-0.11179					
57 -> 85	0.10953					
Excited State	2:	Singlet-?Sym	2.9036 eV	427.01 nm	f=0.0149	<S**2>=0.000
56 -> 58	-0.23497					
56 -> 74	0.14453					
57 -> 58	0.12821					
57 -> 59	0.38399					
57 -> 61	-0.11912					
57 -> 63	-0.12656					
57 -> 66	0.13444					
57 -> 71	-0.13173					
57 -> 74	-0.11107					
57 -> 75	0.37229					
57 -> 86	-0.10981					
Excited State	3:	Singlet-?Sym	3.1142 eV	398.13 nm	f=0.0000	<S**2>=0.000
56 -> 65	0.15704					
56 -> 68	-0.15835					
57 -> 61	0.51478					
57 -> 63	-0.36268					
57 -> 70	-0.10276					

57 -> 73 0.19645

Excited State 4: Singlet-?Sym 3.4500 eV 359.38 nm f=0.0045 <S**2>=0.000

56 -> 58 0.53287

56 -> 62 0.17237

56 -> 67 -0.15775

56 -> 74 -0.22306

57 -> 59 0.16834

57 -> 75 0.17554

Excited State 5: Singlet-?Sym 3.4529 eV 359.07 nm f=0.0045 <S**2>=0.000

56 -> 59 0.53406

56 -> 61 -0.13816

56 -> 63 -0.10004

56 -> 66 0.16520

56 -> 75 0.22914

57 -> 58 0.16537

57 -> 62 0.10083

57 -> 74 -0.17182

Excited State 6: Singlet-?Sym 3.7431 eV 331.23 nm f=0.0001 <S**2>=0.000

56 -> 62 0.17246

56 -> 64 -0.39876

56 -> 65 0.14110

56 -> 67 0.13083

56 -> 69 -0.18502

56 -> 80 0.45869

Excited State 7: Singlet-?Sym 3.8648 eV 320.81 nm f=0.0004 <S**2>=0.000

57 -> 58 -0.15152

57 -> 62 0.24518

57 -> 64 -0.38628

57 -> 65 0.14740

57 -> 69 -0.17025

57 -> 80 0.41917

Excited State 8: Singlet-?Sym 3.9438 eV 314.38 nm f=0.0002 <S**2>=0.000

56 -> 61 0.41479

56 -> 63 -0.26163
56 -> 73 0.12747
57 -> 60 0.11747
57 -> 64 0.14705
57 -> 65 0.30436
57 -> 68 -0.28926

Excited State 9: Singlet-?Sym 4.0030 eV 309.73 nm f=0.0039 <S**2>=0.000
56 -> 58 -0.14954
56 -> 62 0.17539
56 -> 65 -0.12026
56 -> 67 -0.12457
56 -> 74 -0.13286
57 -> 59 0.43848
57 -> 61 0.22266
57 -> 63 0.23123
57 -> 66 -0.19682
57 -> 75 -0.18891

Excited State 10: Singlet-?Sym 4.0173 eV 308.62 nm f=0.0038 <S**2>=0.000
56 -> 59 -0.14239
56 -> 63 -0.18932
56 -> 66 0.13375
56 -> 75 0.13665
57 -> 58 0.41743
57 -> 62 -0.25916
57 -> 64 -0.11842
57 -> 65 0.13283
57 -> 67 0.22861
57 -> 74 0.18056
57 -> 80 0.12302

Excited State 11: Singlet-?Sym 4.1016 eV 302.28 nm f=0.0003 <S**2>=0.000
56 -> 60 0.17322
56 -> 64 0.15130
56 -> 65 0.44005
56 -> 68 -0.41054
57 -> 61 -0.13711

57 -> 63 0.17486

Excited State 12: Singlet-?Sym 4.5928 eV 269.95 nm f=0.0217 <S**2>=0.000

56 -> 58 0.31633
56 -> 62 -0.25659
56 -> 67 0.11646
56 -> 72 -0.11329
56 -> 74 0.34300
57 -> 59 0.11835
57 -> 61 0.18109
57 -> 63 0.20473
57 -> 66 -0.25107

Excited State 13: Singlet-?Sym 4.5955 eV 269.80 nm f=0.0220 <S**2>=0.000

56 -> 59 -0.31679
56 -> 61 -0.15756
56 -> 63 -0.21288
56 -> 66 0.11383
56 -> 71 -0.11432
56 -> 75 0.34652
57 -> 58 -0.11870
57 -> 62 0.27013
57 -> 67 -0.25208

Excited State 14: Singlet-?Sym 5.1514 eV 240.68 nm f=0.0120 <S**2>=0.000

56 -> 58 -0.11561
56 -> 67 0.17050
56 -> 74 -0.34128
57 -> 59 -0.16034
57 -> 61 0.14443
57 -> 63 0.12979
57 -> 66 -0.25588
57 -> 75 0.35423

Excited State 15: Singlet-?Sym 5.1530 eV 240.61 nm f=0.0118 <S**2>=0.000

56 -> 59 0.11512
56 -> 66 0.17507
56 -> 75 -0.34204

57 -> 58 0.15904

57 -> 62 0.19823

57 -> 67 -0.25262

57 -> 74 0.35240

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TDDFT-V-Triplet

Excited State 1: 3.053-?Sym 0.0576 eV 21520.56 nm f=0.0000 <S**2>=2.080

54A -> 59A 0.12033

54A -> 63A -0.10566

54A -> 71A -0.22532

58A -> 59A 0.62332

58A -> 63A -0.40036

58A -> 67A -0.16957

58A -> 71A -0.68966

58A -> 73A -0.24001

58A -> 85A 0.13144

56B -> 57B 0.21205

54A <- 71A -0.10214

58A <- 59A 0.31279

58A <- 63A -0.19531

58A <- 71A -0.32083

58A <- 73A -0.11098

56B <- 57B 0.16333

Excited State 2: 3.031-?Sym 0.5125 eV 2419.31 nm f=0.0002 <S**2>=2.047

58A -> 62A -0.34475

58A -> 64A -0.27294

58A -> 69A 0.10388

58A -> 75A 0.11187

56B -> 57B 0.85047

Excited State 3: 3.016-?Sym 0.5147 eV 2408.85 nm f=0.0004 <S**2>=2.024

54A -> 62A 0.16214

54A -> 64A 0.12300

58A -> 62A 0.62905

58A -> 64A 0.45443

58A -> 65A -0.10808

58A -> 69A -0.15614

58A -> 75A -0.19957
56B -> 57B 0.48680
57A <- 60A -0.11904

Excited State 4: 3.047-?Sym 0.6672 eV 1858.39 nm f=0.0005 <S**2>=2.071
54A -> 65A 0.13062
54A -> 70A -0.10556
54A -> 80A 0.21360
58A -> 62A 0.17010
58A -> 63A -0.18332
58A -> 65A 0.51829
58A -> 70A -0.32924
58A -> 76A 0.19523
58A -> 78A 0.16624
58A -> 79A -0.19067
58A -> 80A 0.56212

Excited State 5: 3.042-?Sym 0.7662 eV 1618.23 nm f=0.0016 <S**2>=2.064
54A -> 62A -0.12922
54A -> 64A 0.15641
54A -> 69A -0.11832
58A -> 61A -0.24650
58A -> 62A -0.55118
58A -> 64A 0.62205
58A -> 69A -0.39970

Excited State 6: 3.082-?Sym 1.5405 eV 804.83 nm f=0.0000 <S**2>=2.125
54A -> 60A 0.13553
58A -> 59A 0.17301
58A -> 60A 0.94237
58A -> 66A -0.11615

Excited State 7: 3.095-?Sym 1.6659 eV 744.24 nm f=0.0000 <S**2>=2.144
58A -> 59A 0.78746
58A -> 60A -0.19267
58A -> 63A 0.39021
58A -> 67A 0.15130
58A -> 71A 0.31562

58A -> 73A 0.10868

Excited State 8: 3.106-?Sym 2.4190 eV 455.99 nm f=0.0303 <S**2>=2.162

57A -> 62A -0.12964
58A -> 59A -0.12114
58A -> 60A -0.10860
58A -> 63A 0.34146
58A -> 65A -0.17960
58A -> 66A -0.52074
58A -> 67A 0.22642
58A -> 68A 0.59519
58A -> 71A -0.24624
58A -> 73A -0.10069

Excited State 9: 3.114-?Sym 2.8084 eV 441.48 nm f=0.0002 <S**2>=2.175

58A -> 59A -0.12184
58A -> 60A 0.13545
58A -> 63A 0.54033
58A -> 66A 0.35255
58A -> 67A 0.35626
58A -> 68A -0.36929
58A -> 71A -0.40764
58A -> 73A -0.15613
58A -> 80A 0.10732

Excited State 10: 3.848-?Sym 2.8984 eV 427.76 nm f=0.0002 <S**2>=3.451

56A -> 62A 0.32552
57A -> 59A -0.10837
57A -> 62A -0.46469
57A -> 64A -0.13389
57A -> 75A 0.12169
58A -> 65A 0.31710
58A -> 67A 0.12863
58A -> 70A 0.14031
58A -> 80A -0.15116
56B -> 58B 0.24040
56B -> 59B -0.18131
56B -> 67B 0.48669

56B -> 76B -0.26682

56B <- 67B 0.11074

Excited State 11: 3.539-?Sym 2.9169 eV 425.06 nm f=0.0003 <S**2>=2.880

56A -> 62A -0.24393

57A -> 59A -0.11232

57A -> 62A 0.24969

58A -> 65A 0.51256

58A -> 66A -0.10990

58A -> 67A 0.21251

58A -> 70A 0.23699

58A -> 80A -0.25776

56B -> 58B 0.42954

56B -> 59B -0.12461

56B -> 67B -0.31595

56B -> 76B 0.16975

Excited State 12: 3.741-?Sym 2.9637 eV 418.35 nm f=0.0014 <S**2>=3.248

56A -> 59A 0.32885

56A -> 63A -0.14584

56A -> 71A -0.27762

57A -> 59A -0.14496

58A -> 65A -0.33454

58A -> 67A -0.11817

58A -> 70A -0.14462

58A -> 80A 0.16654

55B -> 57B -0.21748

56B -> 58B 0.65270

56B -> 59B -0.12135

56B -> 61B -0.11411

Excited State 13: 3.215-?Sym 3.0494 eV 406.58 nm f=0.0001 <S**2>=2.335

56A -> 59A 0.41284

56A -> 63A -0.22428

56A -> 71A -0.38149

56A -> 73A -0.12842

57A -> 59A 0.40191

57A -> 63A -0.13320

57A -> 71A -0.26910

58A -> 65A 0.19830

58A -> 70A 0.10680

58A -> 80A -0.12641

55B -> 57B 0.10738

56B -> 59B 0.43609

Excited State 14: 3.279-?Sym 3.1411 eV 394.72 nm f=0.0002 <S**2>=2.439

56A -> 59A 0.19241

56A -> 71A -0.18293

57A -> 59A -0.25991

57A -> 71A 0.13118

55B -> 57B 0.83229

56B -> 58B -0.13794

56B -> 59B -0.26178

Excited State 15: 3.426-?Sym 3.2049 eV 386.86 nm f=0.0077 <S**2>=2.684

56A -> 59A -0.24184

56A -> 60A -0.14514

56A -> 63A 0.17457

56A -> 71A 0.27016

57A -> 59A 0.18944

58A -> 65A -0.12979

58A -> 80A 0.10900

54B -> 57B 0.16834

55B -> 57B 0.44588

56B -> 58B 0.46533

56B -> 59B 0.47760

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TDDFT-Rea-S_0-Nb

Excited State 1: Singlet-?Sym 3.0355 eV 408.45 nm f=0.0022 <S**2>=0.000

51 -> 53 0.59164

52 -> 53 -0.21507

52 -> 54 -0.29726

Excited State 2: Singlet-?Sym 3.0412 eV 407.68 nm f=0.0326 <S**2>=0.000

51 -> 54 0.57973

52 -> 53 -0.31305

52 -> 54 0.22342

Excited State 3: Singlet-?Sym 3.4474 eV 359.65 nm f=0.0251 <S**2>=0.000
51 -> 53 0.19530
51 -> 54 0.30825
51 -> 56 -0.21363
51 -> 61 0.11359
52 -> 53 0.53005

Excited State 4: Singlet-?Sym 3.4598 eV 358.36 nm f=0.0258 <S**2>=0.000
51 -> 53 0.29314
51 -> 54 -0.20619
51 -> 57 -0.21137
51 -> 62 0.11586
52 -> 54 0.53429

Excited State 5: Singlet-?Sym 4.1053 eV 302.01 nm f=0.0019 <S**2>=0.000
52 -> 56 0.64040
52 -> 59 -0.13821
52 -> 61 -0.14258
52 -> 62 0.11060
52 -> 72 -0.10284

Excited State 6: Singlet-?Sym 4.1353 eV 299.82 nm f=0.0020 <S**2>=0.000
51 -> 56 0.10290
52 -> 57 0.63716
52 -> 61 -0.14912
52 -> 62 -0.16749

Excited State 7: Singlet-?Sym 4.2250 eV 293.45 nm f=0.0002 <S**2>=0.000
52 -> 56 0.10994
52 -> 58 0.10178
52 -> 59 0.63415
52 -> 61 -0.10099
52 -> 62 0.11625
52 -> 72 0.17394

Excited State 8: Singlet-?Sym 4.2991 eV 288.40 nm f=0.0014 <S**2>=0.000

51 -> 57 -0.23592

51 -> 58 0.61427

51 -> 68 -0.10418

51 -> 81 0.19208

Excited State 9: Singlet-?Sym 4.4226 eV 280.34 nm f=0.0000 <S**2>=0.000

52 -> 57 -0.10415

52 -> 58 0.64554

52 -> 59 -0.10973

52 -> 81 0.18320

Excited State 10: Singlet-?Sym 4.8572 eV 255.26 nm f=0.0373 <S**2>=0.000

51 -> 56 -0.34361

51 -> 59 0.47926

51 -> 72 0.11387

52 -> 60 -0.16349

52 -> 67 0.15439

52 -> 71 -0.18090

Excited State 11: Singlet-?Sym 4.9749 eV 249.22 nm f=0.0857 <S**2>=0.000

51 -> 56 0.24479

51 -> 57 0.39827

51 -> 58 0.17949

51 -> 59 0.13267

51 -> 69 -0.15590

52 -> 61 -0.11451

52 -> 69 0.24286

52 -> 70 0.15870

52 -> 77 0.13245

Excited State 12: Singlet-?Sym 4.9831 eV 248.81 nm f=0.0783 <S**2>=0.000

51 -> 56 0.32351

51 -> 57 -0.26338

51 -> 59 0.30153

51 -> 62 0.10400

51 -> 70 -0.14876

52 -> 62 -0.11044

52 -> 65 -0.10575

52 -> 69 0.13698

52 -> 70 -0.24494

52 -> 76 0.12808

Excited State 13: Singlet-?Sym 5.3700 eV 230.88 nm f=0.0011 <S**2>=0.000

51 -> 55 0.12382

51 -> 71 0.10044

52 -> 55 0.64722

52 -> 60 -0.14984

Excited State 14: Singlet-?Sym 5.3734 eV 230.74 nm f=0.0001 <S**2>=0.000

50 -> 53 0.10518

51 -> 55 0.39121

51 -> 60 0.28603

51 -> 67 -0.26683

51 -> 71 0.31495

52 -> 55 -0.20343

Excited State 15: Singlet-?Sym 5.6188 eV 220.66 nm f=0.0000 <S**2>=0.000

51 -> 55 0.55534

51 -> 60 -0.32899

51 -> 67 0.17444

51 -> 71 -0.17687

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TDDFT-Nb-Triplet

Excited State 1: 3.010-?Sym 0.0284 eV 43583.38 nm f=0.0000 <S**2>=2.015

53A -> 54A -1.36619

53A -> 59A -0.18163

53A <- 54A -0.94822

Excited State 2: 3.017-?Sym 0.2874 eV 4313.29 nm f=0.0000 <S**2>=2.026

51B -> 52B 0.98846

Excited State 3: 3.004-?Sym 1.1019 eV 1125.17 nm f=0.0002 <S**2>=2.005

53A -> 54A -0.16384

53A -> 56A -0.37455

53A -> 59A 0.74423

53A -> 61A -0.18166

53A -> 62A -0.46494

Excited State 4: 3.014-?Sym 1.1777 eV 1052.80 nm f=0.0035 <S**2>=2.021

53A -> 55A 0.91601

53A -> 57A 0.34654

53A -> 74A -0.11467

Excited State 5: 3.012-?Sym 1.2694 eV 976.74 nm f=0.0074 <S**2>=2.018

53A -> 56A 0.85427

53A -> 57A -0.26137

53A -> 59A 0.32087

53A -> 62A -0.14561

53A -> 77A 0.10045

53A -> 79A -0.10799

Excited State 6: 3.013-?Sym 1.2882 eV 962.49 nm f=0.0034 <S**2>=2.019

53A -> 55A -0.35547

53A -> 56A 0.24373

53A -> 57A 0.85149

53A -> 59A 0.11195

53A -> 71A -0.10976

53A -> 74A -0.18044

Excited State 7: 3.025-?Sym 2.0707 eV 598.76 nm f=0.0002 <S**2>=2.037

53A -> 56A -0.10744

53A -> 58A 0.37633

53A -> 60A 0.73678

53A -> 63A 0.20598

53A -> 64A 0.44063

53A -> 72A -0.16781

Excited State 8: 3.013-?Sym 2.5042 eV 495.11 nm f=0.0035 <S**2>=2.019

53A -> 58A 0.87906

53A -> 60A -0.43968

Excited State 9: 3.010-?Sym 2.6147 eV 474.18 nm f=0.0060 <S**2>=2.015

53A -> 61A 0.38234

53A -> 62A -0.14420

53A -> 66A 0.82808
53A -> 70A -0.27397
53A -> 76A 0.10226
53A -> 78A -0.11723

Excited State 10: 3.018-?Sym 2.6241 eV 469.27 nm f=0.0302 <S**2>=2.027
53A -> 59A 0.28290
53A -> 61A 0.14199
53A -> 62A 0.35323
53A -> 64A 0.14816
53A -> 65A 0.71187
53A -> 69A 0.44097
53A -> 75A -0.17312

Excited State 11: 3.371-?Sym 2.8809 eV 444.57 nm f=0.0199 <S**2>=2.591
52A -> 54A 0.66510
53A -> 63A 0.56684
53A -> 64A -0.29255
53A -> 67A 0.15561
53A -> 73A 0.16830
53A -> 77A 0.14086
53A -> 79A -0.13849
50B -> 52B 0.13019

Excited State 12: 3.771-?Sym 3.0350 eV 408.51 nm f=0.0047 <S**2>=3.305
52A -> 54A -0.28777
53A -> 63A 0.34558
53A -> 64A -0.13951
50B -> 52B -0.12702
51B -> 53B 0.82479

Excited State 13: 3.067-?Sym 3.1761 eV 390.37 nm f=0.0000 <S**2>=2.101
52A -> 54A -0.35729
53A -> 63A 0.16253
50B -> 52B 0.89550

Excited State 14: 3.041-?Sym 3.1997 eV 387.49 nm f=0.0009 <S**2>=2.062
51A -> 54A -0.50595

51A -> 59A -0.16225

52A -> 55A 0.10280

53A -> 57A 0.15284

53A -> 71A -0.25748

53A -> 74A 0.74019

49B -> 52B 0.10632

Excited State 15: 3.015-?Sym 3.2997 eV 375.74 nm f=0.0006 <S**2>=2.022

53A -> 59A 0.44737

53A -> 61A 0.32202

53A -> 62A 0.65463

53A -> 64A -0.13287

53A -> 65A -0.38834

53A -> 69A -0.22253

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TDDFT-Rea-S_0-Ta

Excited State 1: Singlet-?Sym 2.9627 eV 418.48 nm f=0.0016 <S**2>=0.000

51 -> 53 0.61190

52 -> 54 -0.34194

Excited State 2: Singlet-?Sym 2.9765 eV 416.55 nm f=0.0226 <S**2>=0.000

51 -> 54 0.58738

52 -> 53 -0.37912

Excited State 3: Singlet-?Sym 3.4099 eV 363.60 nm f=0.0236 <S**2>=0.000

51 -> 54 0.36187

51 -> 55 0.22676

51 -> 57 -0.10867

52 -> 53 0.52293

52 -> 56 0.10846

Excited State 4: Singlet-?Sym 3.4344 eV 361.01 nm f=0.0255 <S**2>=0.000

51 -> 53 0.32210

51 -> 56 -0.23456

52 -> 54 0.54383

52 -> 55 -0.11308

Excited State 5: Singlet-?Sym 4.0625 eV 305.19 nm f=0.0031 <S**2>=0.000

51 -> 56 -0.14914
52 -> 55 0.60103
52 -> 56 0.15119
52 -> 57 -0.22382

Excited State 6: Singlet-?Sym 4.0897 eV 303.16 nm f=0.0023 <S**2>=0.000
51 -> 55 -0.16060
52 -> 55 -0.12555
52 -> 56 0.62732
52 -> 57 0.10184
52 -> 59 -0.10445
52 -> 61 -0.10022

Excited State 7: Singlet-?Sym 4.3053 eV 287.98 nm f=0.0018 <S**2>=0.000
51 -> 55 0.35164
51 -> 57 0.56597
51 -> 67 -0.12978
51 -> 82 0.12912

Excited State 8: Singlet-?Sym 4.3295 eV 286.37 nm f=0.0000 <S**2>=0.000
52 -> 56 0.11873
52 -> 59 0.65800
52 -> 74 -0.17250

Excited State 9: Singlet-?Sym 4.4601 eV 277.99 nm f=0.0000 <S**2>=0.000
52 -> 55 0.25588
52 -> 57 0.62693
52 -> 82 0.12860

Excited State 10: Singlet-?Sym 4.9202 eV 251.99 nm f=0.0545 <S**2>=0.000
51 -> 56 0.35582
51 -> 59 0.51489
51 -> 74 -0.10298
52 -> 60 -0.16375
52 -> 73 0.18016

Excited State 11: Singlet-?Sym 5.1407 eV 241.18 nm f=0.1741 <S**2>=0.000
51 -> 55 0.45164

51 -> 57 -0.29975

52 -> 53 -0.19111

52 -> 56 0.11706

52 -> 61 0.12934

52 -> 69 -0.18608

52 -> 78 0.15992

52 -> 80 0.11633

Excited State 12: Singlet-?Sym 5.1751 eV 239.58 nm f=0.1611 <S**2>=0.000

51 -> 56 0.43015

51 -> 59 -0.32584

52 -> 54 0.18602

52 -> 62 -0.13542

52 -> 70 -0.18108

52 -> 77 0.16769

52 -> 79 0.12329

Excited State 13: Singlet-?Sym 5.4457 eV 227.67 nm f=0.0002 <S**2>=0.000

52 -> 58 0.67751

52 -> 60 0.17459

Excited State 14: Singlet-?Sym 5.6125 eV 220.91 nm f=0.0000 <S**2>=0.000

51 -> 58 0.66335

51 -> 73 0.14548

Excited State 15: Singlet-?Sym 5.7252 eV 216.56 nm f=0.0000 <S**2>=0.000

49 -> 54 0.11941

50 -> 53 0.15043

51 -> 58 0.19160

51 -> 60 0.50578

51 -> 68 0.10140

51 -> 73 -0.34793

51 -> 75 -0.12623

==========

TDDFT-Ta-Triplet

Excited State 1: 3.009-?Sym -0.0919 eV -13485.62 nm f=-0.0000 <S**2>=2.013

51B -> 52B -1.07504

51B <- 52B -0.42556

Excited State 2: 3.019-?Sym 0.1012 eV 12252.73 nm f=0.0000 <S**2>=2.029

53A -> 54A	-0.98148
53A -> 58A	-0.20417
51B -> 52B	0.11860
53A <- 54A	-0.15753

Excited State 3: 3.032-?Sym 0.9755 eV 1271.00 nm f=0.0001 <S**2>=2.048

52A -> 74A	-0.10935
53A -> 54A	-0.22521
53A -> 56A	0.33577
53A -> 58A	0.85178
53A -> 61A	0.28536

Excited State 4: 3.024-?Sym 1.1139 eV 1113.03 nm f=0.0029 <S**2>=2.036

53A -> 55A	0.96012
53A -> 57A	0.21242
53A -> 74A	-0.10453

Excited State 5: 3.037-?Sym 1.2403 eV 999.63 nm f=0.0023 <S**2>=2.057

53A -> 55A	-0.23699
53A -> 57A	0.92396
53A -> 74A	-0.21461
51B -> 53B	-0.11105

Excited State 6: 3.010-?Sym 1.2781 eV 970.06 nm f=0.0007 <S**2>=2.015

53A -> 56A	0.90314
53A -> 58A	-0.33725
53A -> 64A	0.10474
53A -> 81A	-0.12257
51B -> 54B	-0.11329

Excited State 7: 3.971-?Sym 2.5444 eV 487.29 nm f=0.0040 <S**2>=3.692

51A -> 55A	-0.12776
52A -> 54A	-0.41367
53A -> 74A	-0.11459
51B -> 53B	0.87814

Excited State 8: 3.022-?Sym 2.6583 eV 471.37 nm f=0.0129 <S**2>=2.034

53A -> 59A	0.95607
53A -> 63A	-0.10736
53A -> 72A	-0.16372
51B -> 54B	-0.10057

Excited State 9: 3.011-?Sym 2.6966 eV 459.78 nm f=0.0159 <S**2>=2.017

53A -> 60A	0.80596
53A -> 63A	0.11243
53A -> 68A	0.11731
53A -> 72A	0.44007
51B -> 54B	0.27096

Excited State 10: 3.048-?Sym 2.9426 eV 421.35 nm f=0.0072 <S**2>=2.072

51A -> 54A	-0.41967
52A -> 54A	0.19077
53A -> 56A	0.12942
53A -> 63A	0.64701
53A -> 64A	-0.25358
53A -> 69A	0.13873
53A -> 72A	-0.19241
53A -> 73A	0.11585
53A -> 74A	-0.29211
53A -> 81A	-0.16076
51B -> 54B	0.20551

Excited State 11: 3.167-?Sym 2.9497 eV 420.33 nm f=0.0016 <S**2>=2.258

51A -> 54A	-0.16665
52A -> 54A	-0.50035
52A -> 58A	-0.21347
53A -> 57A	0.14682
53A -> 63A	0.29965
53A -> 64A	-0.12543
53A -> 69A	-0.30244
53A -> 74A	0.60512
50B -> 52B	-0.10026

Excited State 12: 3.045-?Sym 3.0602 eV 405.14 nm f=0.0025 <S**2>=2.068

53A -> 62A 0.23884
53A -> 67A 0.14644
53A -> 71A -0.20703
50B -> 52B 0.89845
50B -> 58B -0.11088

Excited State 13: 3.052-?Sym 3.0771 eV 402.92 nm f=0.0164 <S**2>=2.079
53A -> 62A 0.58230
53A -> 67A 0.34787
53A -> 71A -0.50939
53A -> 77A -0.15246
53A -> 78A 0.20308
50B -> 52B -0.37280

Excited State 14: 3.021-?Sym 3.1353 eV 395.45 nm f=0.0000 <S**2>=2.032
53A -> 58A -0.23295
53A -> 61A 0.69321
53A -> 65A 0.29532
53A -> 70A -0.50264
53A -> 76A 0.29444

Excited State 15: 3.042-?Sym 3.1697 eV 391.15 nm f=0.0013 <S**2>=2.064
51A -> 54A -0.12498
49B -> 52B 0.94771
49B -> 58B -0.10925
51B -> 54B -0.17275

Table S3. M06-2X/Def2-SVPD calculated vibrational frequencies in the CO-stretching region for various stationary points discussed in the main paper. No scaling factors.

Species	Vibrational Frequencies (cm^{-1})			
Rea-S_0-V	2118.9	2119.1	2138.5	2194.9
Min-T_1-V	2148.7	2155.7	2173.2	2236.9
[CpV(CO)$_3$]^1	2122.3	2130.0	2210.7	
[CpV(CO)$_3$]^3	2087.2	2089.5	2212.3	
Pro-S_0-V	2092.5	2106.6	2154.5	
Rea-S_0-Nb	2092.8	2095.8	2114.3	2194.0
Min-T_1-Nb	2078.5	2092.6	2101.5	2198.0
[CpNb(	2051.	2101.2	2182.0	

$CO)_3]^1$	1			
[CpNb(	2067.	2071.6	2174.2	
$CO)_3]^3$	9			
Pro-S_0-	2078.	2119.4	2168.4	
Nb	2			
Rea-S_0-	2092.	2092.8	2112.5	2194.
Ta	4			2
Min-T_1-	2076.	2076.5	2077.7	2197.
Ta	0			7
[CpTa(	2040.	2087.7	2173.0	
$CO)_3]^1$	5			
[CpTa(	2053.	2057.5	2162.7	
$CO)_3]^3$	4			
Pro-S_0-	2070.	2123.0	2171.6	
Ta	2			

Figure S1 The energy profiles for the photochemical oxidative addition of a $(Me)_3Si–H$ bond to η^5-$CpV(CO)_4$ (**Rea-S_0-V**). The relative energies are obtained at the M06-2X/Def2-SVPD level of theory. The solvent effect (SCRF = PCM, solvent = heptane) was considered using the M06-2X/Def2-SVPD + PCM(solvent = heptane)//M06-2X/ Def2-SVPD method, whose computational results are collected in the parenthesis. All energies (in kcal/mol) are given with respect to the reactant (**Rea-S_0-V**). For the M06-2X-optimized structures for the crucial points, see Figure 2. For more information, see the text.

Figure S2 The energy profiles for the photochemical oxidative addition of a $(Me)_3Si–H$ bond to η^5-$CpNb(CO)_4$ (**Rea-S_0-Nb**). The relative energies are obtained at the M06-2X/Def2-SVPD level of theory. The solvent effect (SCRF = PCM, solvent = heptane) was considered using the M06-2X/Def2-SVPD + PCM(solvent = heptane)//M06-2X/ Def2-SVPD method, whose computational results are collected in the parenthesis. All energies (in kcal/mol) are given with respect to the reactant (**Rea-S_0-Nb**). For the M06-2X-optimized structures for the crucial points, see Figure 4. For more information, see the text.

Figure S3 The energy profiles for the photochemical oxidative addition of a $(Me)_3Si–H$ bond to η^5-$CpTa(CO)_4$ (**Rea-S_0-Ta**). The relative energies are obtained at the M06-2X/Def2-SVPD level of theory. The solvent effect (SCRF = PCM, solvent = heptane) was considered using the M06-2X/Def2-SVPD + PCM(solvent = heptane)//M06-2X/ Def2-SVPD method, whose computational results are collected in the parenthesis. All energies (in kcal/mol) are given with respect to the reactant (**Rea-S_0-Ta**). For the M06-2X-optimized structures for the crucial points, see Figure 6 (Supporting Information). For more information, see the text.

(All geometries were calculated M06-2X/Def2-SVPD)

1. Rea-S_0-V

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	1.993393	1.078507	-2.022706
6	1.970657	0.554085	-1.072060
6	1.918331	-0.854360	-0.893821
1	2.061924	2.223429	0.410734
1	1.908239	-1.597900	-1.684897
6	1.926598	-1.117804	0.504574
1	1.923092	-2.097986	0.971616
6	1.984394	0.128670	1.182740
1	2.017649	0.269904	2.259042
6	2.011567	1.157210	0.209314
23	0.010164	0.001313	0.000095
6	-0.953207	-1.688400	-0.287381
8	-1.486173	-2.682860	-0.457273
6	-0.942321	0.304826	-1.696941
8	-1.473084	0.481668	-2.690976
6	-0.910210	1.721103	0.300408
8	-1.424657	2.723415	0.475738
6	-0.924711	-0.283365	1.710910
8	-1.444167	-0.451967	2.712208

M06-2X/Def2-SVPD = -1590.0449521

2. Min-T_1-V

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.743989	2.038153	2.124550
6	0.418629	1.969983	1.089509
6	-0.938271	1.981878	0.639784
1	2.342660	2.012706	-0.039517
1	-1.817065	2.019407	1.277880
6	-0.927305	1.940219	-0.767295
1	-1.795407	1.940025	-1.421027
6	0.436508	1.903396	-1.194120
1	0.778100	1.910369	-2.226173
6	1.255933	2.002569	-0.047711
23	0.005775	-0.210670	0.006419
6	-2.081287	-0.650159	0.009158
8	-3.173066	-0.957033	0.013062
6	-0.040806	-1.078889	1.876998
8	-0.056794	-1.482562	2.937550
6	2.038083	-0.753658	0.029304
8	3.105517	-1.138206	0.043808
6	-0.021258	-1.187543	-1.810752
8	-0.028964	-1.652454	-2.845995

M06-2X/Def2-SVPD = -1589.9995127

3. TS1-T_1-V

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-0.165019	2.310946	-1.960388
6	0.109447	2.101685	-0.929368
6	1.409837	1.736619	-0.476974

1	-1.778824	2.519208	0.185781
1	2.290600	1.616377	-1.101325
6	1.351270	1.584525	0.930430
1	2.180192	1.332506	1.585713
6	0.014892	1.866500	1.341691
1	-0.347816	1.861951	2.366544
6	-0.727884	2.243319	0.200693
23	0.049549	-0.162931	-0.016348
6	1.828739	-1.130633	-0.101695
8	2.843407	-1.646728	-0.144323
6	-0.245831	-0.886732	-1.929092
8	-0.317959	-1.192298	-3.020482
6	-2.310818	-0.245238	-0.034264
8	-3.407803	-0.508844	-0.085572
6	-0.286115	-1.306387	1.672385
8	-0.390142	-1.861569	2.657482

M06-2X/Def2-SVPD = -1589.99831383

4. T_1/S_0-2-V

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	2.0153532	0.9249834	-2.0497643
6	1.9941893	0.4019977	-1.0977189
6	1.9248760	-1.0080321	-0.9214773
1	2.1064982	2.0697969	0.3837272
1	1.8963210	-1.7489978	-1.7144398
6	1.9341406	-1.2720012	0.4783918
1	1.9113617	-2.2509850	0.9470817
6	2.0084037	-0.0241039	1.1555929
1	2.0409129	0.1151574	2.2326892

6	2.0569039	1.0036942	0.1826210
23	0.0138201	-0.1398283	-0.0242375
6	-0.8909368	-1.8874374	-0.3225647
8	-1.3416070	-2.9218658	-0.5006616
6	-1.0073856	0.4249394	-1.6933235
8	-1.4956533	0.6712045	-2.6909382
6	-0.8916965	2.5677574	0.4459680
8	-1.6490276	3.3857724	0.5979293
6	-0.9904410	-0.1691534	1.7476314
8	-1.4686286	-0.2735973	2.7745962

M06-2X/Def2-SVPD = -1590.0037259200

5. $[\eta^5\text{-CpV(CO)}_3]^1$

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	2.122826	-1.270516	-1.797986
6	2.036088	-0.605726	-0.943080
6	2.047511	-0.996388	0.422084
1	1.847417	1.407558	-1.895484
1	2.152750	-2.011484	0.793843
6	1.908285	0.172759	1.211688
1	1.887585	0.210197	2.297343
6	1.811705	1.289289	0.335993
1	1.712575	2.329465	0.631335
6	1.891043	0.803350	-0.993541
23	-0.021255	-0.066998	-0.018431
6	-1.063735	-1.789866	-0.039436
8	-1.646741	-2.766933	-0.037958
6	-1.284088	0.748120	1.329563
8	-1.997900	1.226441	2.074852

6	-1.304197	0.817395	-1.299829
8	-2.041602	1.320759	-2.005118

M06-2X/Def2-SVPD = -1476.8045318

6. Cpx-S_0-V

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.737801	2.374599	-1.815259
6	1.176460	2.064072	-0.871383
6	2.415198	1.387151	-0.705656
1	-0.325844	2.757036	0.624815
1	3.097353	1.105486	-1.502220
6	2.621223	1.182055	0.688825
1	3.489790	0.716225	1.144161
6	1.507269	1.731481	1.380758
1	1.366504	1.750803	2.456830
6	0.626842	2.277531	0.414142
23	0.821296	-0.024387	0.062638
6	2.068778	-1.464028	-0.391912
8	2.846780	-2.261507	-0.650958
6	0.588510	-1.225728	1.624524
8	0.450742	-1.895346	2.538337
6	0.061897	-0.708871	-1.606880
8	-0.383912	-1.077708	-2.595662
14	-2.421873	0.060082	0.095606
1	-1.016666	0.152564	0.682239
6	-3.622782	0.629355	1.431621
1	-4.634419	0.522923	1.001070
1	-3.492031	1.682255	1.715143
1	-3.581476	0.012003	2.338474

6	-2.570932	1.258247	-1.341412
1	-3.556908	1.151775	-1.817052
1	-1.800564	1.123484	-2.109443
1	-2.498691	2.286436	-0.956095
6	-2.782944	-1.744492	-0.270742
1	-1.963099	-2.254858	-0.790267
1	-3.693946	-1.841297	-0.879910
1	-2.957389	-2.263830	0.683295

M06-2X/Def2-SVPD = -1886.4162541

7. TS1-S_0-V

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.682346	2.178597	0.621398
6	-2.659846	1.147407	0.281351
6	-2.678204	0.001662	1.113477
1	-2.610018	1.345427	-1.951804
1	-2.717231	0.003749	2.198979
6	-2.657082	-1.147972	0.286149
1	-2.677680	-2.177794	0.630119
6	-2.620478	-0.712406	-1.071176
1	-2.608415	-1.353406	-1.947322
6	-2.621998	0.706876	-1.073747
23	-0.711938	0.000197	-0.106474
6	-0.034797	-0.006709	1.700774
8	0.289802	-0.012202	2.798607
6	0.006101	-1.793473	-0.566183
8	0.298078	-2.851364	-0.867423
6	0.003056	1.798781	-0.556680
8	0.295191	2.858468	-0.851227

14	1.949936	0.001786	-0.035893
6	2.692185	-1.503437	0.836420
1	3.779358	-1.340877	0.873185
1	2.514433	-2.444229	0.303897
1	2.335892	-1.604989	1.869449
6	2.687140	1.493762	0.862670
1	2.351204	1.555575	1.905777
1	2.482214	2.447888	0.364954
1	3.777414	1.348414	0.871081
6	2.537875	0.012450	-1.839759
1	2.204465	0.897771	-2.389085
1	2.196223	-0.864670	-2.396958
1	3.640959	0.006680	-1.809607
1	2.100718	0.031454	-4.672087

M06-2X/Def2-SVPD = -1886.2329498

8. $[\eta^5\text{-CpV(CO)}_3]^3$

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	2.023019	0.381666	-2.243275
6	2.006886	0.185314	-1.174938
6	1.978667	-1.096535	-0.562798
1	2.049547	2.236584	-0.287541
1	1.970660	-2.051841	-1.079654
6	1.973160	-0.911648	0.840802
1	1.961528	-1.700541	1.587455
6	1.997523	0.484557	1.100458
1	2.008447	0.950794	2.081544
6	2.022042	1.160021	-0.145765
23	0.008053	0.020702	-0.005656

6	-1.265954	-0.963880	-1.273351
8	-2.007067	-1.503279	-1.946491
6	-1.282969	-0.627904	1.447740
8	-2.039205	-0.980006	2.220876
6	-1.196012	1.649784	-0.195148
8	-1.903538	2.536904	-0.293191

M06-2X/Def2-SVPD = -1476.820634

9. Cpx-T_1-V

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-1.123160	2.509673	1.529502
6	-1.376789	2.130254	0.543118
6	-2.645556	1.631496	0.144193
1	0.548039	2.352729	-0.580355
1	-3.534853	1.578140	0.764876
6	-2.549143	1.243188	-1.225649
1	-3.351953	0.844665	-1.838380
6	-1.221684	1.507079	-1.657230
1	-0.825680	1.323092	-2.652539
6	-0.497143	2.055975	-0.567973
23	-1.153916	-0.101532	-0.005089
6	-2.647899	-1.392840	0.257832
8	-3.563579	-2.064484	0.391028
6	-0.292756	-1.375529	-1.362752
8	0.119621	-2.069781	-2.159366
6	-0.539185	-0.448675	1.904242
8	-0.248674	-0.644299	2.985401
14	2.977385	0.073641	-0.181840
1	2.095167	0.378542	-1.349684

6	4.771079	0.233726	-0.726828
1	5.447293	0.003988	0.109671
1	4.993407	1.252241	-1.073015
1	4.998918	-0.461017	-1.547106
6	2.615249	1.307612	1.196676
1	3.228934	1.083093	2.080546
1	1.560406	1.280722	1.500526
1	2.845933	2.334364	0.878649
6	2.664882	-1.687762	0.409650
1	1.628075	-1.842374	0.736867
1	3.320756	-1.917987	1.263552
1	2.880144	-2.414250	-0.388476

M06-2X/Def2-SVPD = -1886.415529

10. TS2-T_1-V

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.728100	2.267974	0.241936
6	-2.702650	1.191525	0.102243
6	-2.730843	0.211665	1.129988
1	-2.644199	0.974668	-2.128082
1	-2.788437	0.408544	2.196510
6	-2.709515	-1.070593	0.519181
1	-2.739098	-2.026421	1.033177
6	-2.678551	-0.877894	-0.891829
1	-2.651292	-1.661657	-1.643053
6	-2.674242	0.509046	-1.147372
23	-0.734167	0.005032	0.038681
6	-0.002352	0.334931	1.875645
8	0.307649	0.526003	2.955271

6	-0.000417	-1.723209	-0.567817
8	0.310853	-2.795594	-0.821585
6	0.003880	1.421075	-1.115689
8	0.317293	2.339390	-1.724289
14	1.984577	-0.005899	-0.035286
6	2.691716	-1.347495	1.107048
1	3.783439	-1.211758	1.131805
1	2.488597	-2.355964	0.725981
1	2.320104	-1.275501	2.136214
6	2.693200	1.640412	0.592020
1	2.351974	1.892485	1.603500
1	2.456381	2.473450	-0.081329
1	3.788201	1.533577	0.620938
6	2.846413	-0.295028	-1.702192
1	2.616086	0.482139	-2.441994
1	2.613236	-1.274283	-2.138880
1	3.929337	-0.262466	-1.501946
1	0.399348	-0.522950	-2.832967

M06-2X/Def2-SVPD = -1886.3140925

11. T_1/S_0-1-V

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.7847161	2.1627776	0.1486827
6	-2.6575784	1.1297945	-0.1568867
6	-2.9008810	-0.0105300	0.6428237
1	-2.0075049	1.3105511	-2.2993737
1	-3.2094632	-0.0008975	1.6839542
6	-2.6288460	-1.1626958	-0.1291889
1	-2.7266740	-2.1907335	0.2044043

6	-2.2356823	-0.7320967	-1.4356194
1	-1.9656584	-1.3768435	-2.2658376
6	-2.2557809	0.6789504	-1.4528542
23	-0.6542853	0.0081707	0.0393110
6	-0.2700129	0.0123485	1.9935516
8	-0.1157946	0.0181277	3.1215005
6	0.1166019	-1.7929761	-0.1145766
8	0.4627807	-2.8739072	-0.2526071
6	0.0090268	1.8603053	-0.0837288
8	0.2571353	2.9707957	-0.1769093
14	2.0671885	-0.0435595	-0.1367468
6	2.7381578	-1.0171442	1.3488356
1	3.8368017	-1.0014175	1.2932577
1	2.4171193	-2.0660488	1.3474500
1	2.4471704	-0.5674258	2.3072054
6	2.9247651	1.6441837	-0.0305515
1	2.6613884	2.1959899	0.8811236
1	2.6907535	2.2830159	-0.8912965
1	4.0101192	1.4702145	-0.0219436
6	2.7510598	-0.8487107	-1.7096208
1	2.6110709	-0.1834563	-2.5724933
1	2.2897571	-1.8182577	-1.9335141
1	3.8328430	-1.0074200	-1.5805815
1	0.3387756	0.4389706	-2.5374908

M06-2X/Def2-SVPD = -1886.3130495700

12. Pro-S_0-V

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.694618	2.203011	0.576268

6	-2.678544	1.157036	0.285781
6	-2.675563	0.051899	1.169508
1	-2.665069	1.251654	-1.953520
1	-2.680983	0.105964	2.254068
6	-2.657951	-1.134393	0.397266
1	-2.659165	-2.147864	0.786131
6	-2.648492	-0.761380	-0.978441
1	-2.644691	-1.440922	-1.824609
6	-2.661335	0.655588	-1.046644
23	-0.719929	0.000499	-0.076111
6	0.064376	-0.002947	1.702849
8	0.483491	-0.005115	2.767482
6	-0.028207	-1.732880	-0.573673
8	0.285654	-2.769540	-0.941481
6	-0.038486	1.742316	-0.560984
8	0.269663	2.779025	-0.933672
14	1.978463	0.001647	-0.128673
6	2.747285	-1.494490	0.739603
1	3.837375	-1.347376	0.743169
1	2.536622	-2.436728	0.220898
1	2.418580	-1.586155	1.782565
6	2.743104	1.510899	0.720634
1	2.402217	1.625128	1.757539
1	2.543083	2.443465	0.180680
1	3.832251	1.358398	0.740606
6	2.562255	-0.008083	-1.921735
1	2.200211	0.879027	-2.458197
1	2.203006	-0.900802	-2.450410
1	3.661327	-0.006478	-1.951515
1	-0.111378	0.028802	-1.595334

M06-2X/Def2-SVPD = -1886.4049184

13. $[T_1\text{-}V]^*$

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	2.099468	0.927256	1.438177
6	1.106501	0.488095	1.417698
6	0.805326	-0.899902	1.386391
1	-0.224140	2.282534	1.473376
1	1.527976	-1.710143	1.392969
6	-0.610844	-1.039282	1.389988
1	-1.162269	-1.974562	1.398945
6	-1.177019	0.262732	1.423915
1	-2.236876	0.498514	1.448165
6	-0.117040	1.202065	1.441051
23	-0.000513	-0.000033	-0.540581
6	0.141934	-1.723863	-1.475448
8	0.226302	-2.737912	-1.991639
6	1.721282	0.137710	-1.487009
8	2.729604	0.217897	-2.014214
6	-0.143884	1.724348	-1.489743
8	-0.227853	2.729719	-2.020972
6	-1.725142	-0.148397	-1.481625
8	-2.734836	-0.236761	-2.004665

M06-2X/Def2-SVPD = -1589.95618621

14. Rea-S_0-Nb

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.223380	0.001895	2.311909

6	-2.213030	-0.005004	1.225625
6	-2.185870	-1.158158	0.394680
1	-2.275704	2.172892	0.722247
1	-2.183968	-2.189930	0.733766
6	-2.200324	-0.721042	-0.959861
1	-2.212935	-1.359498	-1.838583
6	-2.237418	0.699876	-0.960390
1	-2.270857	1.338269	-1.839060
6	-2.244105	1.139354	0.388055
41	-0.070567	0.001628	0.003944
6	1.066153	-1.650750	-0.563606
8	1.692939	-2.555272	-0.874190
6	1.103367	-0.556219	1.638086
8	1.760208	-0.859374	2.523565
6	1.079484	1.658852	0.552729
8	1.715055	2.561114	0.850210
6	1.054387	0.563550	-1.660503
8	1.672323	0.871893	-2.572196

M06-2X/Def2-SVPD = -703.1117118

15. Min-T_1-Nb

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	2.248851	0.496295	-2.176611
6	2.187903	0.146413	-1.149860
6	1.999490	-1.202012	-0.732671
1	2.491801	2.016791	0.027223
1	1.879674	-2.060609	-1.387495
6	2.000973	-1.224276	0.685650
1	1.883311	-2.103290	1.313248

6	2.190303	0.110487	1.144763
1	2.252146	0.429065	2.181700
6	2.348831	0.940755	0.009953
41	-0.070248	0.002575	0.001484
6	-0.866798	-2.014741	-0.035680
8	-1.505213	-2.961175	-0.053998
6	-1.316021	0.185694	-1.697221
8	-1.966104	0.282747	-2.630427
6	-0.343832	2.173137	0.034168
8	-0.740881	3.242567	0.044692
6	-1.305377	0.108057	1.713195
8	-1.943857	0.157748	2.658147

M06-2X/Def2-SVPD = -703.0556336

16. TS1-T_1-Nb

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-1.243140	-1.838676	-2.201799
6	-1.434118	-1.597260	-1.159571
6	-2.297345	-0.571826	-0.686582
1	-0.182051	-3.090616	-0.063986
1	-2.889525	0.099892	-1.300927
6	-2.273540	-0.603889	0.738197
1	-2.845023	0.037857	1.402121
6	-1.395855	-1.650429	1.134864
1	-1.172541	-1.943375	2.157208
6	-0.894077	-2.271695	-0.035881
41	-0.056354	0.091825	0.007380
6	-0.825101	1.999073	0.021888
8	-1.309500	3.037908	0.024860

6	0.967249	0.712838	-1.750940
8	1.440515	1.065400	-2.727807
6	2.249441	-1.419338	-0.034175
8	3.359752	-1.199593	-0.042072
6	1.005787	0.681741	1.753237
8	1.512750	1.008136	2.722342

M06-2X/Def2-SVPD = -703.053119537

17. T_1/S_0-2-Nb

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.1636607	-0.1584506	2.2561049
6	-2.1455164	-0.1636072	1.1696455
6	-2.0854050	-1.3176097	0.3412063
1	-2.2469502	2.0126538	0.6636957
1	-2.0581312	-2.3485291	0.6813115
6	-2.0990450	-0.8806831	-1.0166290
1	-2.0828260	-1.5195253	-1.8946900
6	-2.1676483	0.5389450	-1.0160234
1	-2.2043944	1.1761039	-1.8956628
6	-2.2057186	0.9793378	0.3317530
41	-0.0081581	-0.1244158	-0.0429469
6	0.8003748	-1.9192962	-0.6506191
8	1.2003771	-2.9368772	-0.9935352
6	1.1701722	-0.3854957	1.7059543
8	1.7557828	-0.5878977	2.6650499
6	0.7456503	2.6320691	0.8772567
8	1.7704876	3.0809747	1.0199567
6	1.1403325	0.7283263	-1.6147301
8	1.7100785	1.1482780	-2.5107933

M06-2X/Def2-SVPD = -703.0534478160

18. $[\eta^5\text{-CpNb(CO)}_3]^1$

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	2.307359	-1.686932	-1.540127
6	2.205681	-0.887335	-0.809862
6	2.201115	-1.043612	0.594942
1	1.998996	0.930270	-2.099189
1	2.318501	-1.980472	1.134114
6	2.018297	0.246622	1.181030
1	2.009137	0.471285	2.243696
6	1.936034	1.199090	0.123987
1	1.834051	2.274831	0.235809
6	2.026403	0.492808	-1.104888
41	-0.033916	-0.195729	0.017846
6	-1.591668	-1.736618	0.041811
8	-2.418633	-2.517033	0.015669
6	-1.159021	1.026103	1.222746
8	-1.791576	1.727517	1.875778
6	-1.159464	0.943041	-1.270569
8	-1.782512	1.611428	-1.964096

M06-2X/Def2-SVPD = -589.8497601

19. $\text{Cpx-S}_0\text{-Nb}$

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.496156	2.385853	-1.983203
6	1.021344	2.150887	-1.061826
6	2.278525	1.495786	-0.958066
1	-0.344391	2.959603	0.514855
1	2.890511	1.158363	-1.788889
6	2.613519	1.402805	0.425009
1	3.526592	0.981309	0.833817
6	1.563901	2.002651	1.171529
1	1.521635	2.105602	2.251643
6	0.584039	2.457140	0.252371
41	0.701514	-0.025086	0.053069
6	1.846433	-1.690075	-0.331755
8	2.469707	-2.628076	-0.555196
6	0.600963	-1.256911	1.735350
8	0.596597	-1.926709	2.664252
6	-0.126499	-1.001721	-1.556658
8	-0.584610	-1.515318	-2.479560
14	-2.487247	0.119774	0.135164
1	-1.093328	0.014854	0.798279
6	-3.389345	0.918702	1.576511
1	-4.453822	1.039579	1.329914
1	-2.978354	1.911492	1.804092
1	-3.315034	0.300418	2.480889
6	-2.599834	1.230298	-1.370002
1	-3.659514	1.440339	-1.576041
1	-2.160231	0.765426	-2.260519
1	-2.098151	2.190450	-1.192191
6	-3.117923	-1.614502	-0.161302
1	-2.661738	-2.074498	-1.045264
1	-4.207221	-1.587092	-0.308324
1	-2.908028	-2.249555	0.709878

M06-2X/Def2-SVPD = -999.4843489

20. TS1-S_0-Nb

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.695596	2.181143	0.661238
6	-2.694291	1.150505	0.318125
6	-2.690012	0.001160	1.149832
1	-2.679904	1.350127	-1.917784
1	-2.693951	0.002666	2.236156
6	-2.694665	-1.150464	0.321325
1	-2.696424	-2.180129	0.667358
6	-2.685123	-0.714662	-1.037912
1	-2.680589	-1.356433	-1.913942
6	-2.684814	0.710897	-1.039915
41	-0.640239	-0.000653	-0.123908
6	0.088530	0.003983	1.771145
8	0.418890	0.007107	2.870119
6	0.128533	-1.902293	-0.569442
8	0.442137	-2.961650	-0.843739
6	0.128058	1.899820	-0.575494
8	0.441277	2.959076	-0.851751
14	2.091180	0.000116	-0.012370
6	2.829222	-1.506655	0.856657
1	3.918353	-1.367921	0.901708
1	2.631382	-2.446768	0.329877
1	2.458429	-1.596051	1.886335
6	2.826119	1.499937	0.870690
1	2.470356	1.564951	1.907560
1	2.609653	2.447660	0.365342
1	3.917345	1.372982	0.896769
6	2.638604	0.006444	-1.840353
1	2.301714	0.896395	-2.380728

1	2.285975	-0.870387	-2.391636
1	3.741559	-0.003732	-1.839302
1	2.525594	0.002357	-4.900508

M06-2X/Def2-SVPD = -999.3008547

21. $[\eta^5\text{-CpNb(CO)}_3]^3$

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.188241	0.516424	2.216229
6	-2.156943	0.251511	1.163084
6	-2.113884	-1.067429	0.635240
1	-2.219292	2.242957	0.143928
1	-2.112404	-1.985794	1.215414
6	-2.106541	-0.973475	-0.780480
1	-2.092994	-1.808291	-1.475357
6	-2.142604	0.403530	-1.128539
1	-2.162491	0.806548	-2.137211
6	-2.170437	1.160200	0.072659
41	0.018100	0.020440	0.008061
6	1.373791	-0.914353	1.331933
8	2.131588	-1.417994	2.022917
6	1.379897	-0.717424	-1.428393
8	2.120377	-1.122989	-2.197261
6	1.289966	1.687342	0.111195
8	1.987266	2.592321	0.155134

M06-2X/Def2-SVPD = -589.8607148

22. Cpx-T_1-Nb

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.978360	2.424504	-1.821712
6	1.198198	2.187924	-0.783750
6	2.469766	1.825240	-0.262129
1	-0.793100	2.433026	0.212493
1	3.394999	1.754228	-0.826189
6	2.320129	1.608946	1.141066
1	3.111283	1.345292	1.836365
6	0.957586	1.839770	1.472836
1	0.517603	1.762402	2.463546
6	0.266335	2.204383	0.287590
41	1.044245	-0.117957	0.012778
6	2.708740	-1.354819	-0.007511
8	3.658689	-1.995400	-0.023867
6	0.150444	-1.366170	1.495738
8	-0.337003	-1.983261	2.320824
6	0.530881	-0.822395	-1.922983
8	0.258350	-1.144199	-2.984180
14	-3.135923	0.082036	0.152248
1	-2.189159	0.482633	1.239068
6	-4.894984	0.408479	0.738811
1	-5.617118	0.132149	-0.043282
1	-5.045216	1.469933	0.978214
1	-5.128185	-0.178122	1.637665
6	-2.781609	1.119716	-1.381651
1	-3.462451	0.833774	-2.195903
1	-1.752106	0.979267	-1.739891
1	-2.931058	2.190696	-1.182743
6	-2.922233	-1.746748	-0.236329
1	-1.927451	-1.962288	-0.650384
1	-3.670992	-2.060041	-0.978637

1	-3.056329	-2.362772	0.663678

M06-2X/Def2-SVPD = -999.4603822

23. TS2-T_1-Nb

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.661647	1.674190	-1.597317
6	-2.688859	0.870636	-0.866708
6	-2.785444	1.020951	0.547930
1	-2.595451	-0.976645	-2.143026
1	-2.834208	1.962947	1.088228
6	-2.824061	-0.277017	1.128704
1	-2.883822	-0.502555	2.190533
6	-2.746530	-1.230326	0.071676
1	-2.737493	-2.311509	0.187683
6	-2.666506	-0.528165	-1.155456
41	-0.660385	0.024936	0.086736
6	0.158904	1.747665	0.948106
8	0.514136	2.696509	1.477354
6	0.153669	-1.755492	0.799008
8	0.508439	-2.741443	1.257705
6	0.176469	0.190433	-1.778835
8	0.540159	0.333366	-2.858642
14	2.110700	-0.025244	0.013372
6	2.744820	-0.117222	1.796992
1	3.842448	-0.042664	1.772792
1	2.483365	-1.071618	2.272501
1	2.361275	0.700087	2.421784
6	2.855729	1.526929	-0.772043
1	2.528403	2.449133	-0.276428

1	2.607836	1.595903	-1.838872
1	3.949952	1.461132	-0.683603
6	2.880627	-1.486476	-0.911815
1	2.639002	-1.466427	-1.983095
1	2.574719	-2.459369	-0.506002
1	3.973770	-1.403548	-0.809839
1	0.223063	-2.356968	-1.695422

M06-2X/Def2-SVPD = -999.38033

24. T_1/S_0-1-Nb

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.9521498	2.1469382	0.1454047
6	-2.8251399	1.1171399	-0.1766405
6	-3.0606674	-0.0379383	0.6108968
1	-2.1825696	1.3324886	-2.3180269
1	-3.3766802	-0.0451685	1.6506326
6	-2.8007385	-1.1816226	-0.1849345
1	-2.9060729	-2.2152294	0.1325474
6	-2.4030852	-0.7332837	-1.4822585
1	-2.1528587	-1.3687267	-2.3274471
6	-2.4189165	0.6863690	-1.4769630
41	-0.6640744	-0.0101330	0.0307257
6	-0.3242973	0.0089044	2.0833539
8	-0.1926661	0.0182134	3.2198426
6	0.2383149	-1.8969058	-0.0598521
8	0.6448565	-2.9631004	-0.1384671
6	0.1433892	1.9156333	-0.0601828
8	0.4409733	3.0183500	-0.1156629
14	2.1555365	-0.0389627	-0.0869315

6	2.8725359	-1.0019788	1.3821895
1	3.9698174	-0.9813264	1.3060303
1	2.5565127	-2.0510620	1.4163359
1	2.5981717	-0.5263914	2.3337816
6	3.0595569	1.6262097	-0.0146536
1	2.8359139	2.1917629	0.8989920
1	2.8398366	2.2644688	-0.8794164
1	4.1350219	1.3964984	-0.0207859
6	2.7693399	-0.8343066	-1.6947887
1	2.5825847	-0.1708148	-2.5505069
1	2.3167558	-1.8106757	-1.9052502
1	3.8579396	-0.9720923	-1.6095936
1	0.2924961	0.6068174	-2.8780917

M06-2X/Def2-SVPD = -999.3732887990

25. Pro-S_0-Nb

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.837191	-2.217969	-0.597783
6	-2.817405	-1.166387	-0.325326
6	-2.789946	-0.075048	-1.227811
1	-2.863838	-1.223704	1.916377
1	-2.769212	-0.148100	-2.311834
6	-2.784115	1.126729	-0.474583
1	-2.781270	2.133597	-0.881473
6	-2.805803	0.775658	0.908711
1	-2.832818	1.469646	1.743481
6	-2.828014	-0.642664	0.999770
41	-0.682972	-0.006046	0.063648
6	0.267926	0.043580	-1.784981

8	0.752331	0.071656	-2.823636
6	0.123622	1.811928	0.678932
8	0.496904	2.804753	1.103367
6	0.131838	-1.844790	0.612610
8	0.514061	-2.843157	1.015837
14	2.158578	-0.000652	0.104714
6	2.935832	1.527383	-0.697978
1	4.027716	1.395483	-0.668932
1	2.695202	2.457161	-0.169249
1	2.640262	1.634225	-1.749368
6	2.923787	-1.476038	-0.803115
1	2.622905	-1.506999	-1.858591
1	2.674421	-2.438328	-0.339221
1	4.017307	-1.358260	-0.770324
6	2.729112	-0.065744	1.903367
1	2.357669	-0.971105	2.401575
1	2.367854	0.806062	2.464898
1	3.827683	-0.073674	1.943764
1	0.007683	-0.054670	1.698992

M06-2X/Def2-SVPD = -999.4793994

26. [T_1-Nb]*

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	2.194238	1.073124	-2.023867
6	2.172512	0.548863	-1.072633
6	2.123099	-0.860476	-0.892926
1	2.255662	2.221347	0.409404
1	2.112539	-1.605226	-1.683351
6	2.128628	-1.122983	0.506046

1	2.124562	-2.103481	0.973534
6	2.182492	0.124712	1.184823
1	2.214329	0.265848	2.261760
6	2.208388	1.154223	0.209669
41	0.017690	0.004587	-0.003428
6	-1.144302	-1.700696	-0.297333
8	-1.784921	-2.634064	-0.458319
6	-1.145694	0.312219	-1.709777
8	-1.796827	0.478458	-2.634876
6	-1.106943	1.740251	0.301275
8	-1.728687	2.684743	0.468277
6	-1.117795	-0.278663	1.723450
8	-1.741493	-0.433298	2.669597

M06-2X/Def2-SVPD = -703.015366541

27. Rea-S_0-Ta

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	2.248204	2.163418	0.747070
6	2.224148	1.139197	0.385553
6	2.185257	0.732693	-0.976837
1	2.283572	-0.051795	2.277733
1	2.187018	1.391841	-1.840191
6	2.185302	-0.690895	-1.008257
1	2.185232	-1.311343	-1.899776
6	2.223554	-1.157480	0.333911
1	2.241884	-2.197279	0.648682
6	2.247461	-0.027880	1.191859
73	0.054380	-0.001013	-0.001526
6	-1.119708	0.021284	-1.730431

8	-1.753438	0.029632	-2.683147
6	-1.092023	1.750959	0.023375
8	-1.705488	2.716437	0.038411
6	-1.094568	-0.017344	1.750838
8	-1.712679	-0.023175	2.713063
6	-1.097328	-1.750172	-0.009632
8	-1.714419	-2.713279	-0.016379

M06-2X/Def2-SVPD = -703.1486657

28. Min-T_1-Ta

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	2.270834	-0.440472	2.186098
6	2.209245	-0.105818	1.154120
6	2.008633	1.233825	0.716823
1	2.535346	-1.990872	0.005501
1	1.879670	2.100265	1.358899
6	2.010667	1.234914	-0.703521
1	1.884865	2.102700	-1.344433
6	2.213021	-0.104132	-1.141892
1	2.278122	-0.437459	-2.174075
6	2.373777	-0.916707	0.005774
73	-0.056600	0.005537	0.001307
6	-0.859415	2.028544	0.010373
8	-1.482446	2.985252	0.011247
6	-1.344284	-0.195587	1.657527
8	-2.033547	-0.312272	2.563891
6	-0.265207	-2.157142	-0.010809
8	-0.586742	-3.252490	-0.015276
6	-1.323804	-0.170317	-1.672680

8	-2.003866	-0.273470	-2.587575

M06-2X/Def2-SVPD = -703.0919529

29. TS1-T_1-Ta

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-1.162820	-1.931455	-2.180090
6	-1.370563	-1.680697	-1.143295
6	-2.283204	-0.687883	-0.691416
1	-0.054688	-3.095802	-0.017628
1	-2.900941	-0.053676	-1.320280
6	-2.265102	-0.694237	0.734685
1	-2.867636	-0.066141	1.384094
6	-1.340842	-1.691455	1.154065
1	-1.107758	-1.953204	2.182761
6	-0.800400	-2.306719	-0.004593
73	-0.068685	0.085296	0.000208
6	-0.881351	1.978578	0.002373
8	-1.395109	3.005074	0.004549
6	0.964077	0.683285	-1.747616
8	1.477925	0.994747	-2.721144
6	2.398323	-1.400473	-0.003508
8	3.479896	-1.070437	-0.006081
6	0.989450	0.692149	1.728912
8	1.517982	1.010413	2.692467

M06-2X/Def2-SVPD = -703.086609146

30. T_1/S_0-2-Ta

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-0.2489702	2.2679676	2.1729652
6	-0.5583873	2.1220511	1.1414943
6	-1.8050199	1.5913609	0.7078416
1	1.2083509	2.8651121	-0.0095591
1	-2.6203993	1.2683944	1.3481974
6	-1.8048002	1.5864436	-0.7190050
1	-2.6200830	1.2591542	-1.3574133
6	-0.5579963	2.1141395	-1.1560284
1	-0.2484715	2.2531023	-2.1883083
6	0.2038646	2.4540974	-0.0083282
73	-0.1151502	-0.0235351	0.0001691
6	-1.6190408	-1.4300585	0.0045564
8	-2.4993413	-2.1668089	0.0066020
6	0.5954303	-0.9914906	1.7428460
8	0.9383154	-1.4873829	2.7151778
6	2.7862723	0.3156231	-0.0003216
8	3.6061527	-0.4628644	0.0025064
6	0.5967239	-1.0038206	-1.7351058
8	0.9409424	-1.5065361	-2.7034234

M06-2X/Def2-SVPD = -703.0866009390

31. $[\eta^5$-$CpTa(CO)_3]^1$

Atomic Number	Coordinates (Angstroms) X	Y	Z

1	2.194623	0.652216	-2.173376
6	2.149426	0.316810	-1.141112
6	2.058589	-1.035707	-0.715743
1	2.340849	2.221286	0.033797
1	1.987383	-1.904188	-1.364580
6	2.050627	-1.054248	0.696507
1	1.971978	-1.938914	1.322152
6	2.135036	0.287345	1.158340
1	2.170300	0.596298	2.199136
6	2.208425	1.143705	0.019377
73	-0.011364	0.148999	-0.001277
6	-1.218504	-0.999279	-1.209556
8	-1.907410	-1.662596	-1.848682
6	-1.221858	-0.988319	1.212570
8	-1.918170	-1.636012	1.859707
6	-1.544893	1.682459	-0.006074
8	-2.366502	2.471082	-0.012247

M06-2X/Def2-SVPD = -589.8830664

32. Cpx-S_0-Ta

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.344509	2.429283	-1.950785
6	0.897569	2.176636	-1.050833
6	2.148657	1.504185	-0.998387
1	-0.405370	2.981124	0.580201
1	2.726133	1.167860	-1.853722
6	2.529044	1.388783	0.370626

1	3.449335	0.949541	0.742994
6	1.512619	1.992188	1.159532
1	1.507490	2.078824	2.241464
6	0.507254	2.471063	0.280597
73	0.575367	-0.022364	0.051148
6	1.639941	-1.741172	-0.375596
8	2.215328	-2.706714	-0.621190
6	0.461907	-1.291023	1.710049
8	0.448193	-1.978909	2.627269
6	-0.302974	-0.977359	-1.547603
8	-0.732578	-1.483177	-2.492184
14	-2.534616	0.149939	0.129108
1	-1.155574	0.031777	0.872723
6	-3.416271	0.972911	1.573185
1	-4.472036	1.140810	1.318298
1	-2.966227	1.946035	1.811510
1	-3.375531	0.345893	2.473652
6	-2.679597	1.265209	-1.371698
1	-3.746837	1.450032	-1.565212
1	-2.237558	0.815757	-2.268550
1	-2.201060	2.237110	-1.191354
6	-3.198075	-1.577309	-0.136826
1	-2.785174	-2.046251	-1.037852
1	-4.294053	-1.540321	-0.233192
1	-2.953204	-2.208362	0.729066

M06-2X/Def2-SVPD = -999.5186066

33. TS1-S_0-Ta

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z

1	-2.592051	2.180639	0.696060
6	-2.595340	1.150193	0.352402
6	-2.587049	0.000286	1.183889
1	-2.586282	1.351031	-1.883814
1	-2.582932	0.001449	2.270237
6	-2.593493	-1.151638	0.355078
1	-2.589261	-2.181246	0.700987
6	-2.587731	-0.715610	-1.004899
1	-2.584987	-1.357002	-1.881031
6	-2.588893	0.711235	-1.006444
73	-0.536201	0.000239	-0.099889
6	0.200698	-0.001328	1.796973
8	0.544178	-0.002608	2.892507
6	0.232886	-1.898233	-0.554743
8	0.555065	-2.954051	-0.836853
6	0.232004	1.900092	-0.552469
8	0.553646	2.956746	-0.833058
14	2.205617	0.000367	-0.004013
6	2.943914	-1.508266	0.860823
1	4.033442	-1.372772	0.902658
1	2.740706	-2.447230	0.333922
1	2.575410	-1.596642	1.891482
6	2.940702	1.499480	0.879530
1	2.587065	1.560194	1.917411
1	2.718861	2.447538	0.377216
1	4.032185	1.375884	0.902164
6	2.744036	0.009210	-1.834359
1	2.403035	0.899786	-2.371503
1	2.388032	-0.867441	-2.384207
1	3.846670	-0.000400	-1.840707
1	2.600623	0.010413	-4.918224

M06-2X/Def2-SVPD = -999.3353257

34. $[\eta^5\text{-CpTa(CO)}_3]^3$

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	2.199954	0.530465	-2.212642
6	2.174592	0.259490	-1.160703
6	2.129561	-1.062327	-0.640140
1	2.244009	2.246063	-0.129562
1	2.119110	-1.977892	-1.224818
6	2.127445	-0.976302	0.776603
1	2.113650	-1.815217	1.466521
6	2.170761	0.399091	1.133425
1	2.193750	0.796074	2.144551
6	2.194805	1.162812	-0.064458
73	-0.007336	0.031034	-0.000195
6	-1.354181	-0.927670	-1.298092
8	-2.093710	-1.455631	-1.993932
6	-1.382880	-0.721025	1.402825
8	-2.143778	-1.132963	2.151733
6	-1.345975	1.636171	-0.118914
8	-2.089975	2.505289	-0.184437

M06-2X/Def2-SVPD = -589.8944892

35. Cpx-T_1-Ta

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-0.793731	2.462627	1.817559
6	-0.988857	2.232763	0.773262

6	-2.256537	1.920287	0.210667
1	1.039982	2.407672	-0.158215
1	-3.200849	1.880381	0.745624
6	-2.070863	1.696455	-1.187621
1	-2.849383	1.458394	-1.906192
6	-0.688768	1.872401	-1.475624
1	-0.221962	1.777606	-2.452493
6	-0.022346	2.210452	-0.267292
73	-0.901807	-0.093620	-0.026554
6	-2.570736	-1.327477	-0.014817
8	-3.525793	-1.964035	-0.006123
6	0.049199	-1.388031	-1.422198
8	0.585065	-2.030533	-2.199984
6	-0.478493	-0.769408	1.921149
8	-0.244614	-1.071870	3.000237
14	3.364895	0.068650	-0.135693
1	2.448226	0.478149	-1.243935
6	5.139690	0.323412	-0.707711
1	5.842481	0.041885	0.089297
1	5.327692	1.373587	-0.969203
1	5.364458	-0.291820	-1.589413
6	3.025294	1.147837	1.372807
1	3.704514	0.872472	2.191248
1	1.996474	1.023677	1.738219
1	3.185789	2.212830	1.151873
6	3.077819	-1.741402	0.286577
1	2.075891	-1.903379	0.706318
1	3.813284	-2.074924	1.031859
1	3.180850	-2.378256	-0.602681

M06-2X/Def2-SVPD = -999.4931513

36. TS2-T_1-Ta

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.637358	1.591916	-1.665794
6	-2.646410	0.818062	-0.905538
6	-2.716219	1.021147	0.504150
1	-2.531494	-1.070020	-2.110186
1	-2.782634	1.979837	1.008728
6	-2.717853	-0.256269	1.132005
1	-2.769084	-0.445624	2.199065
6	-2.648503	-1.246491	0.108644
1	-2.615232	-2.320798	0.259330
6	-2.604240	-0.587439	-1.140666
73	-0.559260	0.054524	0.060066
6	0.309625	1.849126	0.735202
8	0.716986	2.850423	1.116856
6	0.255652	-1.615134	1.015626
8	0.625024	-2.535620	1.586127
6	0.299308	-0.111351	-1.824494
8	0.700015	-0.171744	-2.896193
14	2.242795	-0.034360	0.010972
6	2.873193	0.075791	1.792175
1	3.970491	0.146189	1.770865
1	2.604594	-0.821749	2.364076
1	2.484287	0.955091	2.321253
6	2.983206	1.408234	-0.962951
1	2.671677	2.386084	-0.576583
1	2.714535	1.349107	-2.025749
1	4.079052	1.347049	-0.889283
6	2.983046	-1.605271	-0.735802
1	2.725584	-1.717703	-1.797313
1	2.665492	-2.512496	-0.205499
1	4.078298	-1.528181	-0.657118
1	0.207627	-2.484859	-1.298644

M06-2X/Def2-SVPD = -999.4165889

37. T_1/S_0-1-Ta

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.9536800	2.1470078	0.1459934
6	-2.8302882	1.1176152	-0.1770998
6	-3.0670651	-0.0387141	0.6097389
1	-2.1833919	1.3335050	-2.3179469
1	-3.3805360	-0.0463921	1.6501201
6	-2.8069499	-1.1823583	-0.1869330
1	-2.9074555	-2.2160317	0.1305196
6	-2.4033981	-0.7333631	-1.4823677
1	-2.1534531	-1.3671927	-2.3289656
6	-2.4184933	0.6877616	-1.4763679
73	-0.6628184	-0.0113719	0.0391703
6	-0.3222534	0.0115138	2.0926180
8	-0.1934712	0.0186527	3.2316558
6	0.2344847	-1.9052141	-0.0521597
8	0.6555286	-2.9662615	-0.1415215
6	0.1383340	1.9191428	-0.0526143
8	0.4491249	3.0190488	-0.1196407
14	2.1595049	-0.0390967	-0.0862223
6	2.8742504	-1.0030202	1.3829437
1	3.9713970	-0.9836045	1.3066578
1	2.5547819	-2.0512066	1.4172811
1	2.5968717	-0.5264672	2.3333418
6	3.0609859	1.6270084	-0.0144419
1	2.8356630	2.1927219	0.8986837
1	2.8389867	2.2656333	-0.8786573
1	4.1365812	1.3999921	-0.0207018
6	2.7715379	-0.8353869	-1.6951355
1	2.5806538	-0.1727670	-2.5509390

1	2.3173888	-1.8112669	-1.9048686
1	3.8602039	-0.9740538	-1.6163744
1	0.2966116	0.6142412	-2.9054874

M06-2X/Def2-SVPD = -999.4082239920

38. Pro-S_0-Ta

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.747839	2.266970	0.408068
6	-2.727476	1.193838	0.239669
6	-2.677325	0.197130	1.244830
1	-2.802502	1.035033	-1.994999
1	-2.647711	0.375766	2.316139
6	-2.671423	-1.073709	0.611265
1	-2.663982	-2.036402	1.113385
6	-2.719198	-0.858205	-0.799942
1	-2.755716	-1.628336	-1.564538
6	-2.755762	0.544929	-1.027308
73	-0.577487	0.000307	-0.067360
6	0.374312	-0.053980	1.781014
8	0.859957	-0.084405	2.821336
6	0.238559	-1.833792	-0.665539
8	0.655565	-2.808919	-1.089509
6	0.238813	1.858633	-0.593863
8	0.657708	2.844228	-0.990658
14	2.290538	0.009844	-0.089850
6	3.052558	-1.507066	0.749262
1	4.146418	-1.393155	0.719665
1	2.798814	-2.445176	0.241825
1	2.753145	-1.584858	1.801931

6	3.048067	1.502797	0.794679
1	2.737316	1.555825	1.845934
1	2.804105	2.454326	0.308111
1	4.141836	1.385846	0.774348
6	2.890702	0.038171	-1.879658
1	2.532972	0.934087	-2.404059
1	2.543050	-0.845250	-2.431429
1	3.990232	0.044349	-1.894579
1	0.122045	0.061016	-1.720465

M06-2X/Def2-SVPD = -999.517856

39. $[T_1\text{-}Ta]^*$

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-2.227639	-0.000686	2.315851
6	-2.218225	-0.005191	1.229485
6	-2.194106	-1.158119	0.396993
1	-2.277672	2.173657	0.728060
1	-2.194500	-2.190256	0.735446
6	-2.211037	-0.719441	-0.957579
1	-2.224778	-1.357206	-1.836686
6	-2.244881	0.701626	-0.956172
1	-2.273061	1.341015	-1.834230
6	-2.249264	1.140256	0.392987
73	-0.064848	-0.002309	-0.003708
6	1.096683	-1.645927	-0.567142
8	1.723448	-2.550310	-0.881164
6	1.102125	-0.558721	1.643363
8	1.726937	-0.864053	2.551711
6	1.096677	1.654318	0.541793

8	1.721732	2.562981	0.844462
6	1.066226	0.561934	-1.673545
8	1.671940	0.870508	-2.593498

M06-2X/Def2-SVPD = -703.050918829

40. $[CO]^1$

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	0.000000	0.000000	-0.642693
8	0.000000	0.000000	0.482020

M06-2X/Def2-SVPD = -113.1920504

41. $[CO]^3$

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	0.000000	0.000000	-0.682232
8	0.000000	0.000000	0.511674

M06-2X/Def2-SVPD = -112.9754061

42. $(Me_3)SiH$

Atomic Number	Coordinates (Angstroms) X	Y	Z
14	-0.000676	-0.000533	0.383758
1	-0.000950	-0.000098	1.876530
6	1.040167	-1.445272	-0.224953
1	1.058854	-1.471848	-1.323790
1	0.637271	-2.403920	0.129080
1	2.077131	-1.363407	0.128059
6	0.733471	1.622530	-0.224805
1	0.147460	2.481843	0.128755
1	0.748527	1.652909	-1.323678
1	1.765388	1.748231	0.130154
6	-1.773023	-0.176636	-0.225435
1	-2.398383	0.654376	0.128177
1	-2.223718	-1.113484	0.129459
1	-1.805807	-0.180878	-1.324202

M06-2X/Def2-SVPD = -409.5900221