Electronic Supplementary Information (ESI)

Dehydrogenation reaction of triethylamine by an electrophilic terminal phosphinidene complex

Arif Ali Khan, Tim Kalisch, Arturo Espinosa Ferao,* and Rainer Streubel*

Table of Contents

Experimental Procedures

All manipulations were carried out under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried and degassed according to standard protocols. Tetrahydrofuran (THF), diethyl ether, petrol ether and n-pentane were dried over sodium wire/benzophenone, toluene and triethylamine over sodium and further purified by subsequent distillation. All spectra were recorded on a Bruker Avance 300 spectrometer at 25 °C. The ^{1}H and ^{13}C NMR spectra were referenced to the residual proton resonances and the ^{13}C NMR signals of the deuterated solvents and ^{31}P NMR spectra were referenced to 85% H_3PO_4 , respectively. NMR data were recorded in $CDCl_3$ solutions (295 K) at 50.3 MHz (^{13}C), 81.0 MHz (^{31}P) and 200 MHz (^{1}H), using TMS and 85% H3PO4 as standard references; J/Hz. Melting points were determined in one-side melted off capillaries using a Büchi Type S apparatus and are uncorrected. Elemental analyses were carried out on a Vario EL gas chromatograph. Mass spectrometric data were collected on a Kratos Concept 1H Spectrometer. IR spectra of all compounds were recorded on a Thermo Nicolet 380 FT-IR spectrometer with an attenuated total reflection (ATR) attachment or a Bruker Alpha Diamond ATR FTIR spectro-meter.

1 NMR spectra

1.1 [{$(Me_3Si)_2HCP(H)((CH_3)HCN(C_2H_5)_2)$}$W(CO)_5$] (**4**)

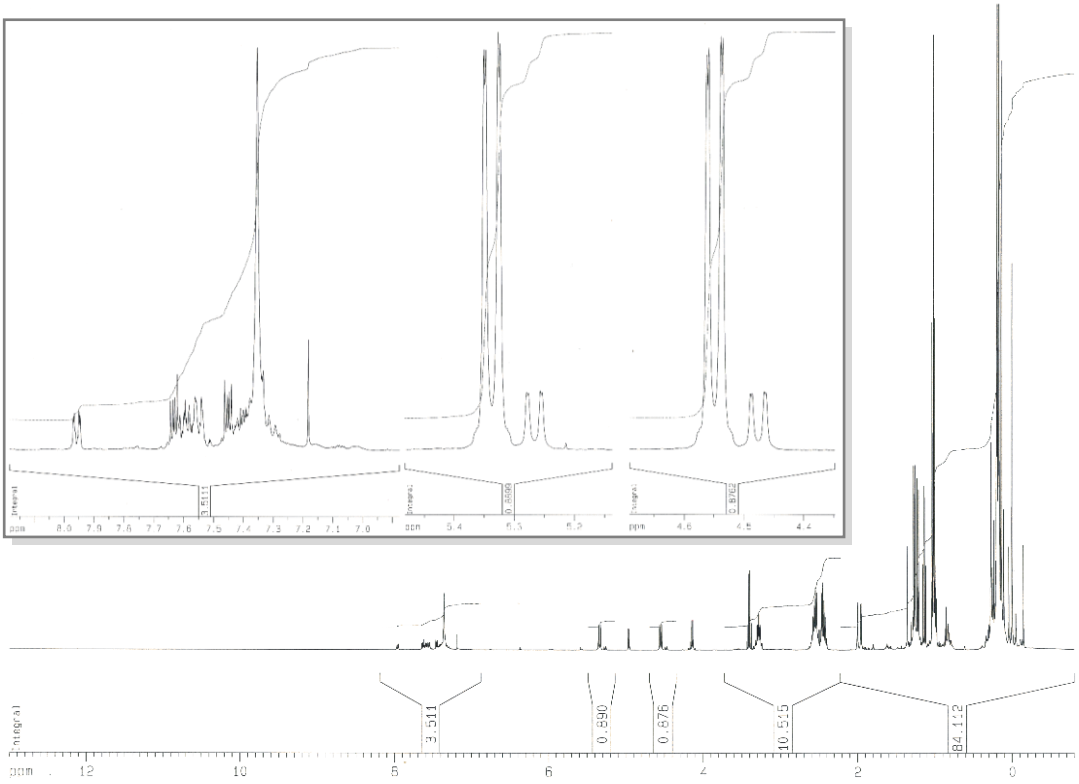

Figure S1. ^{1}H NMR spectrum of **4**.

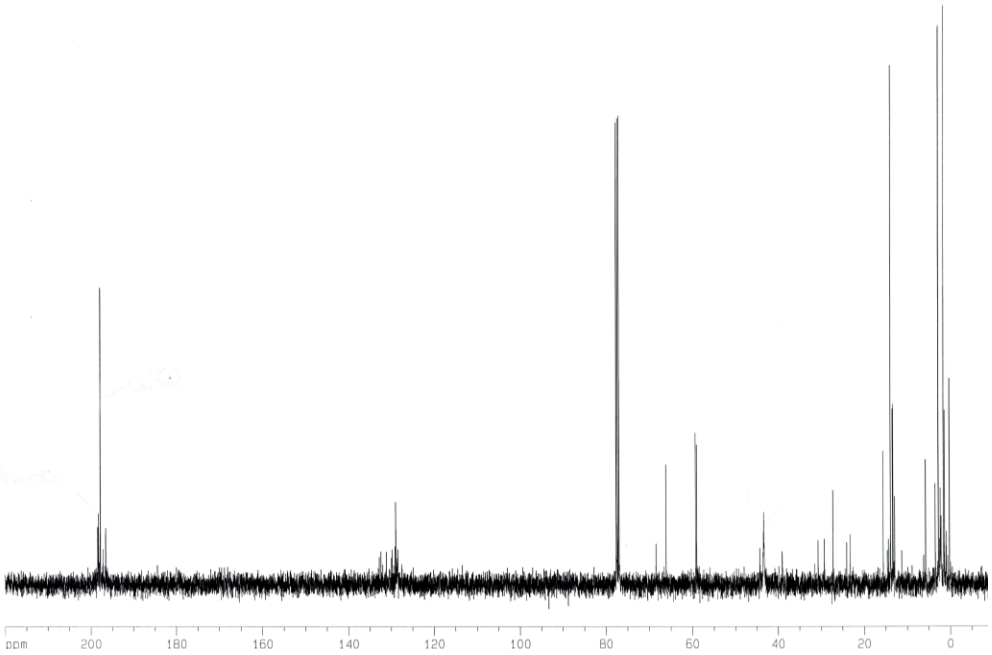

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **4**.

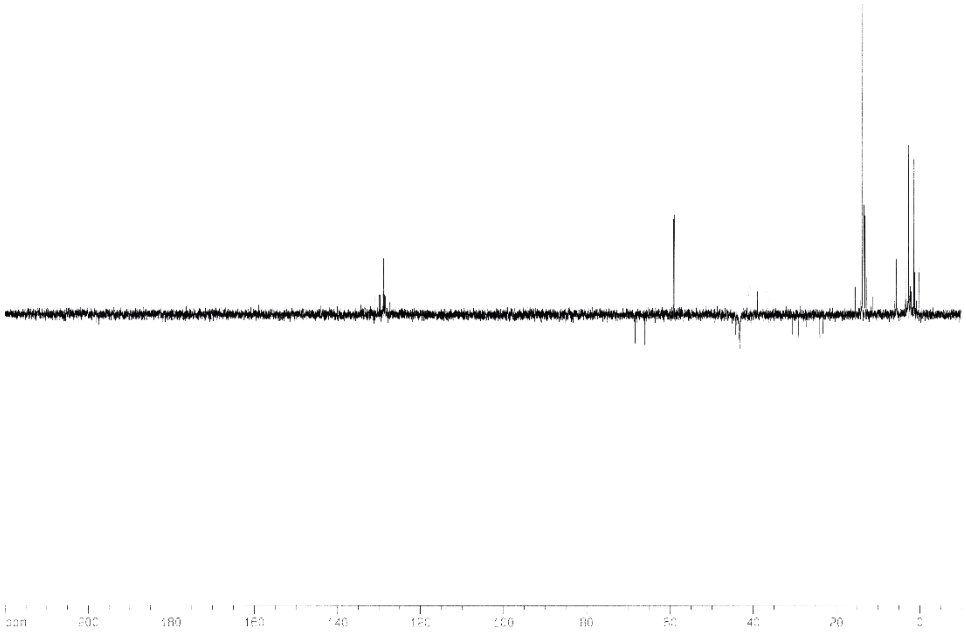

Figure S3. ^{13}C dept135 NMR spectrum of **4**.

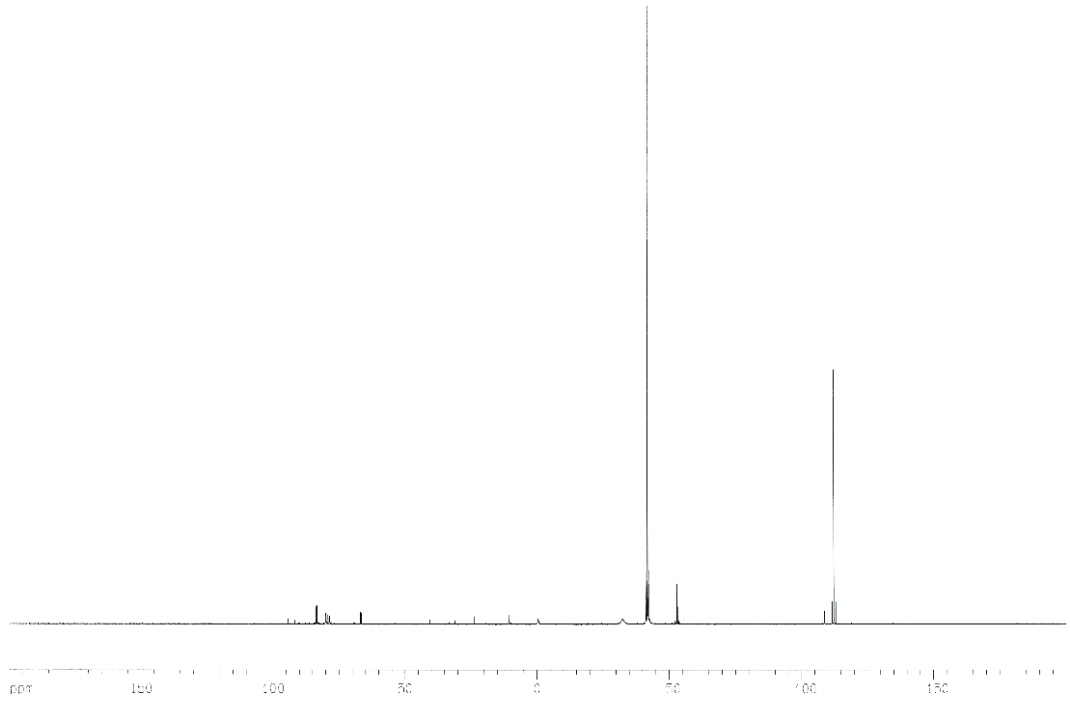

Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of **4**.

1.2 $[\{(Me_3Si)_2HCPH_2\}W(CO)_5]$ (**5**)

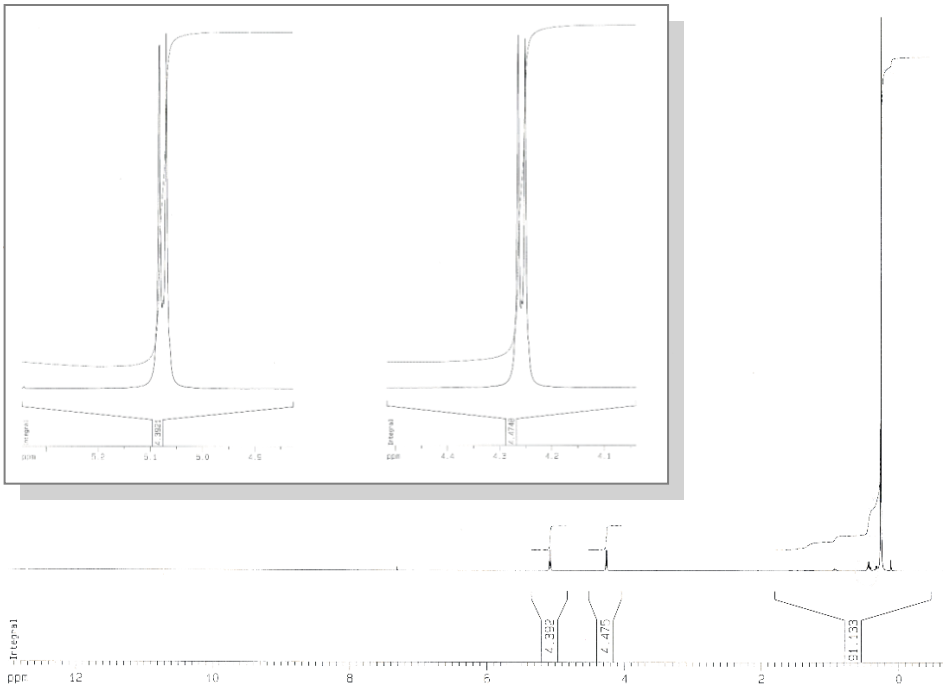

Figure S5. ^{1}H NMR spectrum of **5**.

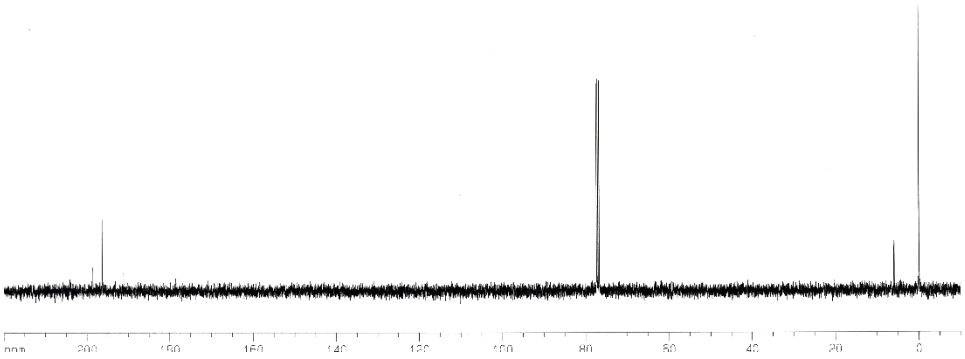

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **5**.

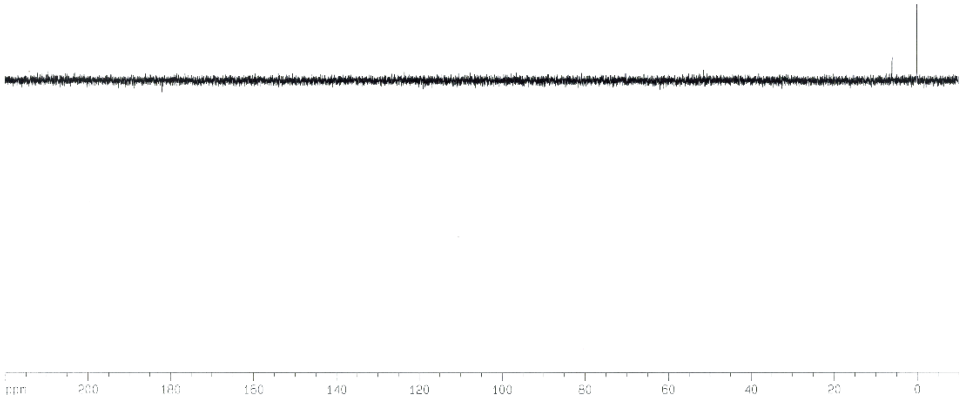

Figure S7. ^{13}C dept135 NMR spectrum of **5**.

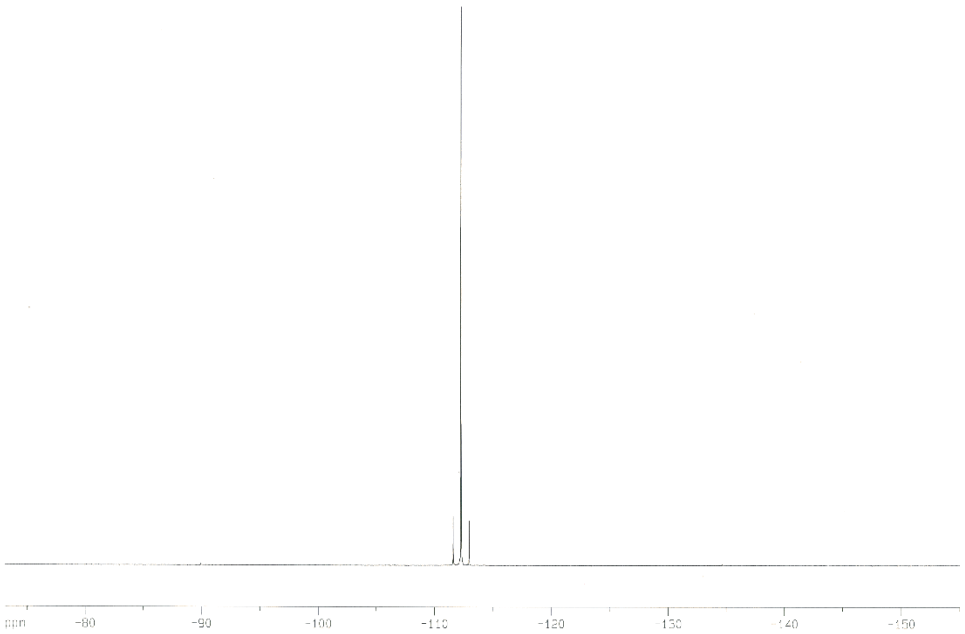

Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of **5**.

Computational Details

DFT calculations were performed with the ORCA electronic structure program package.[1] All geometry optimizations were run in redundant internal coordinates. All optimizations were performed in the gas phase with redundant internal coordinates and tight convergence criteria using the B3LYP functional[2] together with the def2-TZVP basis set[3,4] and speeded up by means of the fast and accurate "chain of spheres" RIJCOSX algorithm.[5] The latest Grimme's semiempirical atom-pairwise dispersion correction based on tight binding partial charges (DFT-D4) was included in all calculations.[6] Harmonic frequency calculations verified the nature of the computed species as minima, featuring none or only one negative eigenvalues for minima or transition states (TS), respectively. The later were checked by performing intrinsic reaction coordinate calculations.[7] Energy values were corrected for the Gibbs free energy correction term at the optimization level and obtained by the DLPNO method[8] for the "coupled cluster" level with single, double as well as triple perturbatively introduced excitations (CCSD(T)).[9] Solvent effects (toluene) were taken into account only for NMR calculations via the Conductor-like Polarizable Continuum Model (CPCM).[10] Isotropic values (σ_{Iso}) for the ^{31}P NMR magnetic shielding tensor were computed using the Gauge Including Atomic Orbital (GIAO) method,[11] at the CPCM(toluene)/PBE0/IGLOIII(C,H,O,N,P)-def2TZVPPecp(W) level. The expected chemical shifts δ^P were estimated through a linear equation $\delta^P = 279.4 - 0.9029 \cdot \sigma_{Iso}$, which in turn was obtained from a linear regression ($R^2 = 0.9963$) of twelve reference compounds (Figure S1), as reporte elsewhere.[12]

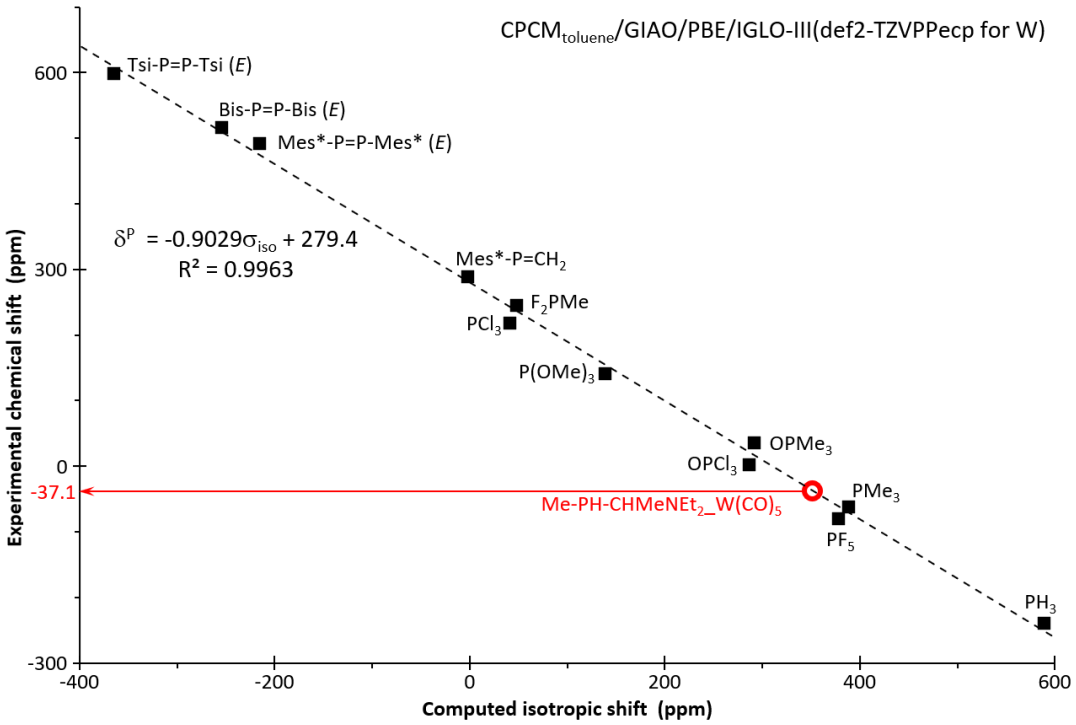

Figure S9. Linear regression fit of experimentally reported ^{31}P chemical shift values and computed magnetic isotopic shift.

1.3 Computed structures.

Cartesian coordinates (in Å), and G correction (G-E) (in hartrees) for minima and transition states were computed at the optimization B3LYP-D3/def2-TZVP(ecp) level. Electronic energies (in hartrees) are quoted at the DLPNO-CCSD(T)/def2-TZVPP(ecp) level. Imaginary frequencies are obtained upon frequency calculation (at the optimization level).

1' E= -1337.46339422434 au
ZPE = 0.18043622 au
G_{corr} = 0.12848859 au

P-0.1698240.075562-0.262336
C0.074258-0.322882 1.500860
H0.889016-1.043610 1.588288
H0.3632940.585993 2.031701
H-0.831302-0.7356831.942182
W1.6560491.096633-1.626193
C3.1546001.959167 -2.698319
O4.0037972.452729 -3.291695
C1.8569802.561857 -0.191351
O1.9635303.374943 0.608942
C3.010935-0.088627-0.618847
O3.749640-0.753602-0.050567
C1.423606-0.390600-3.053588
O1.290147-1.211063-3.836881
C0.2214912.223059 -2.596684
O-0.5974012.828973-3.117536
C-1.8906600.064029-0.611014
N-1.399238-1.075333-0.890431
C-3.1710430.724663-0.699784
C-3.2834712.062795-0.316170
C-4.2889130.033445-1.182934
C-4.5068392.709934-0.416054
H-2.4093372.585271 0.050874
C-5.5070500.684853-1.279672
H-4.185904-1.002438-1.478749
C-5.6160502.021739-0.897700
H-4.5957563.747533-0.122717
H-6.3740440.156583-1.654366
H-6.5699292.527131-0.978082

TS(1'→2') E= -1337.42087296224 au
ZPE = 0.17810074 au
G_{corr} = 0.12750991 au
ν = -209.58 cm^{-1}

P0.2034200.608116 0.620471
C0.879422-0.942387 1.354936
H1.392379-1.595537 0.651451
H1.604397-0.615042 2.111908
H0.093722-1.493746 1.871192
W1.4933181.303277-1.311667
C2.5969431.915410 -2.972986
O3.2199462.221776 -3.880114
C1.6089493.208080 -0.502290
O1.6541884.258186 -0.054511
C3.2099220.700944 -0.321502
O4.1317300.350181 0.255166
C1.333697-0.624768-2.075111
O1.253607-1.692030-2.465723
C-0.2844391.880739-2.204627
O-1.2760522.204518-2.671725
C-2.486756-0.517869-0.784169
N-1.643458-1.299924-0.689528
C-3.4994330.480675-0.891956
C-3.5222511.532037 0.030022
C-4.4402090.419047-1.924041
C-4.4905402.516695-0.086758
H-2.7739501.569545 0.810362
C-5.4029851.410441-2.028155
H-4.405151-0.396329-2.633378
C-5.4294842.456819-1.111581
H-4.5107543.334536 0.621203
H-6.1318281.368463-2.826587
H-6.1816003.230132-1.199023

2' E= -1013.52405102709 au
ZPE = 0.07757558 au
G_{corr} = 0.03339619 au

P-0.0368800.031532-0.384646
C-0.447725-0.0730611.423349

H0.437110-0.107141 2.058388
H-1.0033790.837195 1.655700
H-1.092063-0.9275741.632671
N0.854721-1.464761-0.451124
C1.433989-2.442858-0.669950
W1.8371071.790685-0.788830
C3.2779863.184272 -1.067553
O4.1050273.969053 -1.213968
C0.8907592.997998 0.598596
O0.3569633.647138 1.376559
C2.8791030.866135 0.721212
O3.4222250.298886 1.558183
C2.7055390.502169 -2.122309
O3.171341-0.272481-2.835317
C0.6872412.602435 -2.305420
O0.0479493.041521 -3.146816
C2.156928-3.621063-0.941577
C3.187081-3.596560-1.896258
C1.846903-4.806118-0.254905
C3.890372-4.760152-2.157237
H3.418359-2.675672-2.412293
C2.571346-5.953978-0.523847
H1.050490-4.812019 0.476383
C3.589099-5.934840-1.473885
H4.682719-4.747939-2.893557
H2.339484-6.868208 0.005857
H4.148993-6.837287-1.680762

PhCN E= -323.901541250721 au
ZPE = 0.09900529 au
G_{corr} = 0.06978108 au

N0.895108-2.021448-0.010605
C1.535616-2.906639-0.377215
C2.329354-4.004830-0.832278
C3.015470-3.913329-2.047649
C2.418063-5.169372-0.062619
C3.782750-4.981872-2.485630
H2.940425-3.008645-2.635191
C3.188249-6.231518-0.510934
H1.884459-5.230215 0.875938
C3.869785-6.140184-1.720264
H4.313077-4.910816-3.426054
H3.256901-7.132443 0.084398
H4.468717-6.972491-2.066586

TS(2'+PhCN**→6')** E= -1337.43127406355 au
ZPE = 0.17783013 au
G_{corr} = 0.12630376 au
ν = -28.05 cm^{-1}

P0.3216810.568262 0.638976
C0.985643-1.008710 1.328229
H1.426168-1.677319 0.590772
H1.773029-0.709442 2.032413
H0.217616-1.533344 1.896078
W1.5955311.268702-1.314941
C2.6829531.887117 -2.978522
O3.2957312.197820 -3.892030
C1.7266623.163199 -0.487031
O1.7770924.208138 -0.026698
C3.3199540.650578 -0.349242
O4.2461400.289491 0.214665
C1.398082-0.654626-2.071849
O1.285409-1.724733-2.449821
C-0.1954051.851084-2.172986
O-1.2017722.169680-2.613349
C-2.494182-0.333499-0.728694
N-1.583361-1.025389-0.576372
C-3.5735730.584464-0.873160
C-3.6938061.627569 0.051570
C-4.4767310.463539-1.932875
C-4.7226642.544909-0.090172
H-2.9750381.710220 0.855775
C-5.5012901.388029-2.061290
H-4.365304-0.343369-2.643932
C-5.6248222.426055-1.142924
H-4.8194743.355696 0.619513
H-6.2024591.301108-2.880553
H-6.4250573.146757-1.250272

6' E= -1337.44554676438 au
ZPE = 0.18043627 au
G_{corr} = 0.12640932 au

P-0.0368800.031532-0.384646
C-0.447725-0.0730611.423349
H0.437110-0.107141 2.058388
H-1.0033790.837195 1.655700

H-1.092063-0.9275741.632671
N0.854721-1.464761-0.451124
C1.433989-2.442858-0.669950
W1.8371071.790685-0.788830
C3.2779863.184272 -1.067553
O4.1050273.969053 -1.213968
C0.8907592.997998 0.598596
O0.3569633.647138 1.376559
C2.8791030.866135 0.721212
O3.4222250.298886 1.558183
C2.7055390.502169 -2.122309
O3.171341-0.272481-2.835317
C0.6872412.602435 -2.305420
O0.0479493.041521 -3.146816
C2.156928-3.621063-0.941577
C3.187081-3.596560-1.896258
C1.846903-4.806118-0.254905
C3.890372-4.760152-2.157237
H3.418359-2.675672-2.412293
C2.571346-5.953978-0.523847
H1.050490-4.812019 0.476383
C3.589099-5.934840-1.473885
H4.682719-4.747939-2.893557
H2.339484-6.868208 0.005857
H4.148993-6.837287-1.680762

NEt_3 E= -291.876399292323 au
ZPE = 0.20459928 au
G_{corr} = 0.17166695 au

N-0.2908631.171897-2.017631
C0.3845980.189171 -2.832298
H1.4569150.286833 -2.637728
H0.100487-0.811200-2.480267
C0.1450630.241510 -4.348991
H0.738361-0.528746-4.849498
H-0.9036140.055584-4.587357
H0.4191601.210257 -4.767838
C0.3985542.393799 -1.675827
H-0.2083002.910065-0.925669
H1.3427922.135501 -1.178874
C0.7171473.369546 -2.818867
H1.1908004.271699 -2.421881
H1.4084162.922341 -3.535249
H-0.1827493.665006-3.359156
C-1.7310561.130039-1.918065
H-2.0362770.088335-2.055495
H-2.0188961.399181-0.893271
C-2.5323872.017827-2.882367
H-3.6043991.855664-2.739594
H-2.3326653.075195-2.700504
H-2.2898931.804214-3.923830

2'·NEt_3 E= -1305.17102950181 au
ZPE = 0.28252926 au
G_{corr} = 0.22589466 au

P-1.328235-0.3167050.474042
C0.139983-1.410942 0.136559
H1.101254-0.899232 0.126739
H0.158729-2.133465 0.958880
H0.008322-1.978727-0.786218
W-0.6381611.4733102.111959
C-0.1047692.876045 3.507570
O0.2199383.659926 4.279341
C0.4322970.013043 3.112375
O1.017487-0.814439 3.643808
C1.0327611.855116 0.983962
O1.9708602.027141 0.343429
C-1.7761992.830666 1.067559
O-2.4319563.562340 0.472932
C-2.3355700.987155 3.204429
O-3.2715400.717662 3.802419
N-0.1669201.718687-2.522492
C1.1665061.158192 -2.743140
H1.8971811.936045 -2.525375
H1.3475860.361360 -2.017086
C1.3618250.633442 -4.161921
H2.3624330.211449 -4.274907
H0.640196-0.151704-4.395993
H1.2388401.432867 -4.893311
C-0.2445983.141414-2.210715
H-1.2435763.366233-1.850360
H0.4448403.372104 -1.392472
C0.0750324.017813 -3.417544
H0.0139165.071212 -3.138665
H1.0826323.831358 -3.792709
H-0.6304983.831938-4.228708
C-1.1766300.836306-2.197968
H-0.984182-0.140178-2.641734
H-1.1385230.525782-0.999579
C-2.6164701.266708-2.382698
H-3.2708000.446027-2.092267
H-2.8764772.127593-1.771074
H-2.7973121.513729-3.430751

TS(2'·NEt3**→3')** E= -1305.17368210578 au
ZPE = 0.28366429 au
G_{corr} = 0.22850529 au
ν = -101.77 cm^{-1}

P-0.560377-0.3740070.856901
C1.204784-0.549808 0.370080
H1.2547140.032401 -0.561427
H1.936467-0.149512 1.070047
H1.441554-1.584525 0.117737
W-0.8394671.3462622.540092
C-1.1229212.636994 4.157137
O-1.2516803.323804 5.060039
C0.4358320.231999 3.741454
O1.157487-0.379231 4.380175
C0.8185472.342254 1.809628
O1.7330192.865321 1.367511
C-2.0678002.503521 1.316902
O-2.7330983.132607 0.636188
C-2.5212880.279003 3.112612
O-3.454759-0.3109303.401947
N-0.0261551.268599-2.320751
C0.7534570.481888 -3.257585
H1.7974710.789317 -3.146923
H0.710104-0.568944-2.943882
C0.3648270.541030 -4.741107
H1.053575-0.071391-5.328788
H-0.6398650.145901-4.899301
H0.3936681.558002 -5.131838
C0.4345102.608118 -2.005795
H-0.2449583.011560-1.250521
H1.4144482.531538 -1.519872
C0.5581993.612291 -3.160186
H0.8783114.583116 -2.773624
H1.3053713.287098 -3.885883
H-0.3862313.749480-3.686379
C-1.4492991.001317-2.238189
H-1.591949-0.057845-2.466153
H-1.7648191.124799-1.194964
C-2.3912511.844137-3.107686
H-3.4201921.500688-2.975130
H-2.3582082.895149-2.817586
H-2.1418291.775267-4.166567

3' E= 1305.21206194427 au
ZPE = 0.28997806 au
G_{corr} = 0.23663275 au

P-0.0489310.033428-0.063148
C1.804553-0.039745-0.024822
H2.3150320.921862 0.052414
H2.026501-0.592602 0.891141
H2.224694-0.611624-0.852426
W-0.7811411.4780581.978395
C-1.3193832.380446 3.715317
O-1.6113362.894360 4.700932
C0.4229610.207569 3.075816
O1.095366-0.479969 3.698377
C0.8302502.709153 1.677390
O1.7440063.370311 1.455477
C-1.9908002.794655 0.974042
O-2.6662903.544344 0.420059
C-2.3422550.128736 2.091489
O-3.194227-0.6354362.118115
N-0.2480491.056346-1.780130
C0.4596070.221182 -2.812799
H1.5162770.467034 -2.734364
H0.340381-0.810017-2.479160
C-0.0010110.325267-4.260463
H0.630535-0.340968-4.851299
H-1.028884-0.011341-4.387256
H0.0923091.324713 -4.676448
C0.3391262.432300 -1.637164
H-0.3590102.999933-1.031347
H1.2424912.313526 -1.046503
C0.6987003.200026 -2.902976
H1.1025294.164523 -2.589363
H1.4755472.700038 -3.480604
H-0.1512553.392581-3.552156
C-1.7447071.044511-1.960337
H-1.9968280.038975-2.291083
H-2.1634771.158889-0.963019
C-2.3654172.097257-2.865485
H-3.4434591.927100-2.870029
H-2.2058583.104236-2.483667
H-2.0183502.047609-3.894605

TS(3'→7') E= -1305.12683280014 au
ZPE = 0.28283136 au
G_{corr} = 0.22941848 au
ν = - 770.51 cm^{-1}

P0.2025730.368084 -0.161475
C2.0318930.353616 -0.112394
H2.4622041.348871 -0.015490
H2.287398-0.199047 0.794119
H2.448995-0.162132-0.973704
W-0.7658431.3564691.985911
C-1.4345532.028345 3.786076
O-1.7970272.412565 4.803677
C0.213529-0.192351 2.949389
O0.764957-1.040495 3.484500
C0.9242022.526127 2.088004
O1.8648653.181606 2.094598
C-1.7252932.926164 1.069327
O-2.2487403.809996 0.556227
C-2.4474500.184799 1.715855
O-3.380975-0.4520461.532779
N-0.1833631.220380-1.795267
C0.4411220.188175 -2.733763
H1.5031820.420299 -2.765935
H0.084983-0.769517-1.133603
C-0.1335580.075584-4.123521
H0.466578-0.674756-4.643219
H-1.159975-0.297834-4.137951
H-0.1069380.983459-4.746179
C0.3527612.636828 -1.814988
H-0.3531103.268591-1.279053
H1.2747032.627800 -1.237501
C0.6533443.199876 -3.192774
H1.0924774.191089 -3.064500
H1.3742172.577232 -3.719757
H-0.2332283.303990-3.811926
C-1.6902221.159381-1.862729
H-1.9215820.110322-2.039260
H-2.0619551.419502-0.874746
C-2.3771232.050739-2.882754
H-3.4481571.850158-2.819892
H-2.2361313.107090-2.656634
H-2.0585601.858307-3.903131

7' E= -1305.13658421199 au
ZPE = 0.28430565 au
G_{corr} = 0.23033848 au

P0.0907740.360006 -0.155322
C1.856012-0.056447-0.150967
H2.4624920.832317 0.019122
H2.008346-0.735393 0.689655
H2.115581-0.552155-1.083499
W-0.7458281.4606031.958569
C-1.3565132.208665 3.756233
O-1.6941872.618960 4.770562
C0.4707880.130718 2.968099
O1.153454-0.595954 3.529472
C0.8324802.775474 1.817659
O1.7213173.488264 1.692831
C-1.9508112.838345 1.013365
O-2.6111783.622038 0.498306
C-2.2795180.076850 1.929430
O-3.113356-0.7040411.868664
N-0.1740101.148462-1.835076
C0.5289400.245031 -2.811685
H1.5699050.568118 -2.808564
H-0.474009-0.861669-0.556368
C-0.0212570.225243-4.219272
H0.640024-0.427353-4.793706
H-1.014334-0.226419-4.294264
H-0.0644751.183040-4.769316
C0.3438392.584200 -1.702907
H-0.3824853.158524-1.131459
H1.2503782.519330 -1.102009
C0.6871883.268323 -3.011712
H1.1559404.225794 -2.776734
H1.3953632.673040 -3.584522
H-0.1836063.463632-3.630574
C-1.6787751.085303-1.993797
H-1.8767860.061969-2.304073
H-2.1117651.225400-1.003452
C-2.3224502.083956-2.937619
H-3.3922711.867956-2.957326
H-2.2094263.108816-2.585912
H-1.9455812.008322-3.953519

TS(7'→8') E= -1305.1349845068 au
ZPE = 0.28394230 au
G_{corr} = 0.23073652 au
ν = -99.35 cm^{-1}

P0.0795000.367757 -0.136764
C1.839197-0.066857-0.142728
H2.4532420.804547 0.081614
H1.982980-0.798806 0.653530
H2.093545-0.512014-1.103440
W-0.7485921.4627441.978269
C-1.3490872.208235 3.780466
O-1.6799472.615481 4.798352
C0.4797470.128971 2.969434
O1.169994-0.603598 3.513489

C0.8261992.781155 1.828530
O1.7127793.495892 1.698009
C-1.9615052.835485 1.035140
O-2.6257943.615561 0.519197
C-2.2799260.076452 1.957707
O-3.112497-0.7062491.901661
N-0.1641101.156324-1.855985
C0.5447340.281605 -2.822869
H1.5815530.612484 -2.834011
H-0.496784-0.846243-0.547779
C-0.0205250.192112-4.219728
H0.648902-0.461964-4.782406
H-1.003356-0.284557-4.267609
H-0.0940031.131623-4.798650
C0.3536162.587784 -1.706458
H-0.3681293.150562-1.117565
H1.2673082.513750 -1.117374
C0.6803343.291777 -3.009514
H1.1491664.247475 -2.767751
H1.3826902.705979 -3.599174
H-0.1977593.492597-3.616099
C-1.6675041.096538-2.013096
H-1.8729260.070607-2.308891
H-2.0975471.250722-1.023556
C-2.3113772.084552-2.968327
H-3.3800671.863168-2.991832
H-2.2048343.112358-2.623584
H-1.9290192.003261-3.981894

8' E= -1305.17355871244 au
ZPE = 0.28222808 au
G_{corr} = 0.22544529 au

P-0.179195-0.668731-0.007954
C1.686583-0.821709-0.032660
H2.1112140.067734 -0.506117
H2.129012-0.893828 0.960736
H1.993875-1.695062-0.611955
W-0.7934621.1172661.857698
C-1.1372792.263563 3.480570
O-1.3188102.899840 4.423518
C0.333214-0.163377 3.044707
O0.976188-0.853088 3.692404
C0.8923312.117316 1.300454
O1.8302402.664669 0.905888
C-1.8721992.487116 0.808256
O-2.4583163.334864 0.275752
C-2.495215-0.0354992.096921
O-3.433299-0.6898882.165123
N-0.1722851.862965-2.548287
C0.7238681.049392 -2.993727
H1.7416001.423596 -2.960837
H-0.449904-1.9134700.614987
C0.485210-0.343323-3.364266
H1.382885-0.806384-3.763207
H0.174745-0.843925-2.404033
H-0.345391-0.475548-4.057364
C0.2389743.201722 -2.054411
H-0.5530973.548911-1.397377
H1.1265513.060710 -1.441866
C0.4974374.188136 -3.183513
H0.8066335.142966 -2.757207
H1.2968143.838042 -3.839004
H-0.3938164.356514-3.786633
C-1.6049531.520056-2.442593
H-1.7392480.516102-2.827860
H-1.8241341.480866-1.376730
C-2.5091382.512594-3.157105
H-3.5381542.167030-3.057220
H-2.4592543.505780-2.713454
H-2.2742282.581531-4.220583

TS(2'·NEt_3**→8')** E= -1305.16876879688 au
ZPE = 0.28109099 au
G_{corr} = 0.22372198 au
ν = - 422.92 cm^{-1}

P-1.354772-0.3573610.444072
C0.129204-1.448048 0.131331
H1.079238-0.916496 0.082788
H0.183867-2.138040 0.977346
H-0.004574-2.052110-0.768661
W-0.6390601.4755142.104113
C-0.0890332.878646 3.472472
O0.2467303.671269 4.234204
C0.4192440.007664 3.107066
O0.999255-0.822331 3.641815
C1.0176731.851669 0.967584
O1.9515672.036542 0.318243
C-1.7648982.816966 1.044334
O-2.4136023.542685 0.427854
C-2.3315530.998075 3.209404
O-3.2644130.733468 3.815377
N-0.1496371.706247-2.448969
C1.1826571.136848 -2.694191
H1.9166021.886616 -2.405988
H1.3240370.291348 -2.019869

C1.3856030.707036 -4.142703
H2.3837560.284111 -4.267775
H0.661375-0.056084-4.433930
H1.2820391.550524 -4.825212
C-0.2299533.147066-2.204546
H-1.2144173.379245-1.813093
H0.4900453.398131 -1.423339
C0.0445493.969489 -3.458997
H-0.0437235.031213-3.224263
H1.0506553.796763 -3.843004
H-0.6702103.731085-4.248085
C-1.1765260.865899-2.261546
H-0.980294-0.131733-2.644244
H-1.2228730.414026-0.892441
C-2.6065711.316380-2.372864
H-3.2605590.485219-2.117215
H-2.8404522.143149-1.707304
H-2.8107781.626579-3.401448

TS(8'→4') E= -1305.17589101063 au
ZPE = 0.28307331 au
G_{corr} = 0.22734591 au
ν = -143.74 cm^{-1}

P-0.149277-0.4901370.004512
C1.725848-0.606633-0.022336
H2.1391880.343928 -0.369224
H2.162456-0.803784 0.956926
H2.056881-1.391878-0.707217
W-0.7875551.2313641.934731
C-1.1922472.379472 3.542970
O-1.4085303.020723 4.476079
C0.402261-0.035228 3.075697
O1.077096-0.739286 3.674405
C0.8527862.316548 1.404505
O1.7719922.911905 1.033350
C-1.9363092.455638 0.795132
O-2.5793193.178908 0.153155
C-2.4373780.013484 2.210914
O-3.351860-0.6706192.308432
N-0.2168451.731198-2.576795
C0.6563010.899979 -3.005013
H1.6883791.203342 -2.861873
H-0.380849-1.7453600.624332
C0.389172-0.427422-3.592617
H1.293110-0.832065-4.040748
H0.071680-1.070556-2.756749
H-0.411827-0.409306-4.331264
C0.2354302.999100 -1.943269
H-0.5617873.318881-1.280797
H1.0952702.759879 -1.323269
C0.5751104.069955 -2.967838
H0.9052314.964976 -2.439831
H1.3856163.748181 -3.624409
H-0.2844424.334230-3.582236
C-1.6683501.452272-2.569899
H-1.8282070.505706-3.073465
H-1.9215381.301813-1.521482
C-2.4981112.559598-3.197550
H-3.5437222.253407-3.166881
H-2.4222813.492777-2.642789
H-2.2231742.732278-4.239275

4' E= -1305.24074248088 au
ZPE = 0.28522463 au
G_{corr} = 0.23056204 au

P0.0449510.022115 -0.362889
C1.384718-1.223701-0.181503
H2.329730-0.706404-0.011278
H1.176148-1.838282 0.693130
H1.476503-1.866948-1.053884
W-0.4364141.3160261.784078
C-0.7771612.290484 3.531335
O-0.9698272.847250 4.515482
C0.8245000.045128 2.809624
O1.510450-0.650372 3.407303
C1.1703972.528095 1.341674
O2.0764563.177760 1.075249
C-1.7740852.622168 0.915695
O-2.5497713.356757 0.502263
C-2.0114900.018683 2.098532
O-2.879680-0.7138612.237031
N-0.5359861.878053-2.400535
C0.4503430.902851 -1.992900
H1.3674651.450877 -1.763050
H-1.002418-0.815564-0.801435
C0.760923-0.088290-3.117393
H1.629781-0.704441-2.890135
H-0.081074-0.753524-3.316852
H0.9676390.475939 -4.027176
C-0.2962053.249131-1.958804
H-1.2456823.782018-1.968570
H0.0501073.275739 -0.921525
C0.7063113.978497 -2.845150
H0.8745644.993044 -2.476986
H1.6718393.467789 -2.855806

H0.3426234.031932 -3.872302
C-1.9217261.433985-2.485996
H-1.9129650.366067-2.708340
H-2.4540491.546439-1.530929
C-2.7033532.145559-3.584160
H-3.7207271.752442-3.635833
H-2.7768103.217817-3.398543
H-2.2210852.000907-4.552034

NMe_3 E= -174.163028734229 au
ZPE = 0.11974666 au
G_{corr} = 0.09346260 au

N0.1341760.903706 -1.927265
C0.9277350.021963 -2.762691
H0.8979590.303867 -3.831468
H1.9693910.041185 -2.437726
H0.561809-1.002306-2.674027
C0.6394622.263392 -1.954741
H0.0583512.888846 -1.274891
H1.6801742.278590 -1.626493
H0.5923192.717813 -2.961673
C-1.2732130.846871-2.275150
H-1.635660-0.178754-2.187294
H-1.8496341.472219-1.591247
H-1.4737721.192337-3.306171

TS(8'·NMe_3→**9'**·$Et_2NCH{=}CH_2$**)** E= -1479.33098644275 au
ZPE = 0.40140957 au
G_{corr} = 0.33843655 au
ν = -1352.02 cm^{-1}

P-1.7950560.313163-0.629484
C-2.077578-1.453500-1.191212
H-1.125349-1.877392-1.515459
H-2.475680-2.097532-0.407490
H-2.766005-1.478692-2.039406
W-0.3300770.1883251.595281
C0.658524-0.140573 3.317838
O1.216390-0.356677 4.304230
C0.855423-1.056031 0.469636
O1.496467-1.705484-0.231611
C1.0029531.700410 1.275299
O1.7757142.557117 1.185726
C-1.6479871.574225 2.328441
O-2.4005522.388660 2.642556
C-1.654916-1.3221752.099249
O-2.401130-2.1395652.394803
N-0.0855074.779753-0.864641
C0.7380524.092212 -1.633641
H1.5003984.704512 -2.106799
H-3.1048420.539327-0.124644
C0.7284882.724769 -1.915016
H1.7116552.349839 -2.190208
H0.1769382.066619 -1.249411
H0.0362242.398955 -3.079211
C0.1079476.220392 -0.675397
H0.2547026.396257 0.393397
H1.0357186.494391 -1.177218
C-1.0399747.077154-1.193595
H-0.7880338.131863-1.071810
H-1.2233516.887931-2.252519
H-1.9625586.891705-0.644746
C-1.1481434.131350-0.078526
H-0.7782873.165901 0.255943
H-1.3026584.742940 0.810158
C-2.4533733.939620-0.838014
H-3.1812273.478377-0.170477
H-2.8626294.882390-1.201060
H-2.3113703.260720-1.674850
N-0.4896391.815607-4.153154
C-0.0886290.403187-4.044624
H0.9966200.340357 -3.976184
H-0.530473-0.006565-3.138379
H-0.429301-0.162394-4.916189
C0.1196492.488638 -5.302416
H-0.1539493.543673-5.288494
H1.2041522.403355 -5.236667
H-0.2163822.046001-6.244161
C-1.9521491.964367-4.114898
H-2.3129971.506470-3.192075
H-2.2062813.023733-4.123196
H-2.4109971.480065-4.982272

9'·$Et_2NCH{=}CH_2$ E= -1479.34156833087 au
ZPE = 0.40629933 au
G_{corr} = 0.34408805 au

P-1.5201350.100250-0.730898
C-1.781263-1.621753-1.434117

H-0.806035-2.088375-1.586781
H-2.355565-2.268494-0.771221
H-2.294739-1.585050-2.399664
W-0.572850-0.1978291.727814
C0.069918-0.530270 3.607419
O0.425876-0.730701 4.686786
C0.731268-1.564939 0.910660
O1.452872-2.310280 0.415049
C0.8570381.253782 1.545191
O1.6674392.073523 1.495057
C-1.9224261.228264 2.317756
O-2.6811752.044261 2.607870
C-2.027044-1.6514361.938838
O-2.841690-2.4515982.045485
N0.0997515.094400 -1.110059
C0.9256554.324544 -1.851468
H1.4956514.890634 -2.582799
H-2.8973140.390842-0.513839
C1.1144092.981718 -1.787594
H1.9520112.567138 -2.333147
H0.6597912.353645 -1.035883
H-0.1401802.317013-3.065158
C0.0542946.535876 -1.309004
H0.3342947.030136 -0.372173
H0.8194976.795431 -2.042077
C-1.3029227.057092-1.772621
H-1.2598908.138830-1.914521
H-1.5952336.597058-2.718850
H-2.0817446.849437-1.038235
C-0.6414224.534657 0.021031
H0.0186663.851008 0.557481
H-0.8610745.361422 0.698324
C-1.9327363.819633-0.363272
H-2.4708313.522605 0.536211
H-2.5823394.467381-0.954787
H-1.7288532.909163-0.926330
N-0.6099981.947877-3.945017
C-0.1760610.531048-4.092081
H0.9089280.505402 -4.161883
H-0.5055710.002679-3.198990
H-0.6235580.114617-4.993204
C-0.1201352.801886-5.052751
H-0.4112043.831735-4.859259
H0.9641762.732780 -5.097911
H-0.5550892.461319-5.990373
C-2.0837032.051210-3.762430
H-2.3391871.467599-2.876311
H-2.3434273.096010-3.609668
H-2.5772051.664569-4.653197

TS(9'·$Et_2NCH{=}CH_2$**→5'**·$Et_2NCH{=}CH_2$·NMe_3**)** E= 1479.33085496962 au
ZPE = 0.40149315 au
G_{corr} = 0.33875284 au
v = -1364.55 cm^{-1}

P-1.4091010.085502-0.877561
C-1.231531-1.566719-1.745700
H-0.210500-1.664380-2.119631
H-1.424926-2.417616-1.093521
H-1.912160-1.624401-2.598592
W0.2178430.023827 1.238033
C1.390098-0.267059 2.852706
O2.045690-0.461165 3.781508
C-0.284673-1.9832551.372945
O-0.542778-3.0938461.483667
C1.612786-0.296932-0.223740
O2.308012-0.397621-1.139135
C0.8363571.963248 1.333442
O1.2229233.045905 1.471135
C-1.4802850.593013 2.236439
O-2.4637450.984009 2.688595
N-0.8028524.701967-0.489035
C0.2075734.377685 -1.274161
H0.8366875.222539 -1.538708
H-2.687045-0.161312-0.307855
C0.5424673.125000 -1.792518
H1.5994373.046671 -2.035689
H0.1415122.249647 -1.288882
H0.0025432.828523 -3.046832
C-0.8980536.058597 0.060326
H-0.7316875.987248 1.138996
H-0.0721346.635809-0.354444
C-2.2184706.762495-0.219775
H-2.1682437.782956 0.163282
H-2.4230926.807793-1.290585
H-3.0550526.267441 0.272193
C-1.7474423.698956 0.027068
H-1.2224882.752567 0.124653
H-2.0300704.013835 1.031895
C-2.9762133.504981-0.850538
H-3.6008422.725926-0.413573
H-3.5678554.414951-0.945178
H-2.6850953.166130-1.842029
N-0.3135832.249246-4.197522
C-1.7639172.007370-4.224807
H-2.0269291.423473-3.340174
H-2.2873612.962596-4.204466
H-2.0466831.464928-5.132028
C0.4436920.986566 -4.168761
H1.5037141.203125 -4.046952
H0.1018490.398836 -3.320391

H0.2907620.425008 -5.094073
C0.1354483.147079 -5.264338
H-0.4142344.085973-5.202451
H1.1991943.348876 -5.140495
H-0.0306142.701753-6.249342

5' E= -1014.54480034475 au
ZPE = 0.09790460 au
G_{corr} = 0.05302436 au

P0.005538-0.035173 0.034697
H-0.180380-1.424941-0.123635
H-0.3354430.339878-1.282109
C1.8358950.081131 -0.027624
H2.1197341.132236 -0.074233
H2.244516-0.339950 0.890802
H2.249303-0.446268-0.885947
W-1.2020471.0793311.946455
C-2.1587881.972419 3.506889
O-2.6961522.477210 4.384058
C0.4520852.266642 2.278895
O1.3772632.916302 2.460253
C-1.9620852.477533 0.626959
O-2.3728543.235778-0.124473
C-2.850545-0.1219061.602915
O-3.762078-0.7856531.411705
C-0.397762-0.3647493.182230
O0.066894-1.175112 3.844174

Et_2N-CH=CH_2 E= -290.661558106319 au
ZPE = 0.18170522 au
G_{corr} = 0.14880788 au

N0.0484360.074177 -0.361091
C1.4113140.057172 -0.204440
H1.8682101.026239 -0.379322
C2.200836-0.982577 0.105802
H3.267993-0.834766 0.170257
H1.827168-1.980533 0.283855
C-0.6414061.351274-0.414184
H-0.0212142.047990-0.983221
H-1.5629091.219427-0.987501
C-0.9590491.945792 0.958361
H-1.4811512.900064 0.855221
H-1.5947251.275615 1.540546
H-0.0413862.115221 1.524350
C-0.730395-1.121881-0.092648
H-0.308410-1.6446630.772616
H-1.737963-0.8142470.193746
C-0.800794-2.064241-1.293262
H-1.363067-2.966630-1.042087
H-1.294078-1.576033-2.135865
H0.198714-2.359602-1.612626

TS(8'→5'+$Et_2NCH=CH_2$**)** E= -1305.17469646197 au
ZPE = 0.28049685 au
G_{corr} = 0.22344905 au
ν = -89.70cm^{-1}

P-0.198145-0.8856620.052141
C0.167419-2.572390 0.735450
H1.216779-2.610891 1.028562
H-0.440822-2.7927851.613722
H-0.009599-3.340362-0.018465
W-0.0210971.0093601.817168
C-0.0561482.392869 3.291812
O-0.1015663.178470 4.131623
C1.610273-0.018979 2.563328
O2.521649-0.613561 2.921899
C1.2983862.244544 0.861110
O2.0532412.999627 0.416593
C-1.5903081.857877 0.826203
O-2.4536582.307969 0.207443
C-1.293776-0.1948152.929332
O-1.980452-0.8696183.547107
N-0.3596552.507865-2.445938
C0.7451571.800997 -2.350512
H1.5839822.328793 -1.916570
H-1.573015-1.066231-0.253307
C0.8900320.414453 -2.635807
H1.9274680.123300 -2.772746
H0.545890-0.197168-1.628428
H0.2450030.000976 -3.404592
C-0.3999613.897317-1.968807
H-1.1945843.965090-1.224609
H0.5410234.090255 -1.457883
C-0.6220194.912316-3.082245
H-0.5810095.918161-2.662111
H0.1490974.829949 -3.849815
H-1.5971744.792712-3.554987
C-1.6068491.920524-2.957368

H-1.7030560.920937-2.535347
H-2.4242522.510801-2.548137
C-1.6805351.874136-4.480613
H-2.6149641.399317-4.783535
H-1.6512062.873785-4.912254
H-0.8571471.299155-4.903843

References

1 F. Neese. ORCA – an Ab Initio, DFT and Semiempirical SCF-MO Package. D-45470 Mülheim/Ruhr: Max Planck Institute for Bioinorganic Chemistry. Version 4.2.1. Web site http://www.cec.mpg.de/forum/portal.php F. Neese, *WIREs Comput. Mol. Sci.* **2017**, *8*, e1327.

2 a) C. Lee, W. Yang and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B*, **1988**, *37*, 785–789; b) A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.*, **1993**, *98*, 5648–5652.

3 F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

4 A. Schäfer, C. Huber and R. Ahlrichs, Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *J. Chem. Phys.*, **1994**, *100*, 5829–5835.

5 F. Neese, F. Wennmohs, A. Hansen and U. Becker, Efficient, approximate and parallel Hartree–Fock and hybrid DFT calculations. A 'chain-of-spheres' algorithm for the Hartree–Fock exchange. *Chem. Phys.*, **2009**, *356*, 98–109.

6 a) E. Caldeweyher, C. Bannwarth and S. Grimme, Extension of the D3 dispersion coefficient model. *J. Chem. Phys.*, **2017**, *147*, 34112; b) E. Caldeweyher, S. Ehlert, A. Hansen, H. Neuegebauer, S. Spicher, C. Bannwarth and S. Grimme, A generally applicable atomic-charge dependent London dispersion correction. *J. Chem. Phys.*, **2019**, *150*, 154122.

7 K. Ishida, K. Morokuma and A. Komornicki, The intrinsic reaction coordinate. An ab initio calculation for HNC→HCN and $H^- + CH_4 \rightarrow CH_4 + H^-$. *J. Chem. Phys.*, **1977**, *66(5)*, 2153-2156.

8 C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, Natural triple excitations in local coupled cluster calculations with pair natural orbitals. *J. Chem. Phys*. **2013**, *139*, 134101.

9 J. A. Pople, M. Head-Gordon, K. Raghavachari, Quadratic configuration interaction. A general technique for determining electron correlation energies. *J. Chem. Phys*. **1987,** *87*, 5968.

10 a) V. Barone , M. Cossi, Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model. *J. Phys. Chem. A*, **1998**, *102*, 1995-2001; b) M. Cossi, N. Rega, G. Scalmani, V. Barone, Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J. Comp. Chem.*, **2003**, *24*, 669-81.

11 T. Ziegler, G. Schreckenbach, Calculation of NMR shielding tensors using gauge-including atomic orbitals and modern density functional theory. *J. Phys. Chem.* **1995**, *99*, 606–611.

12 A. Gese, S. Kermanshashian, G. Schnakenburg, Z. Kelemen, L. Nyulaszi, A. Espinosa Ferao, R. Streubel "Towards a 1,4-diphosphinine-based molecular CPS-ternary compound", *Inorg. Chem.*, **2021**, *60(17)*, 13029-13040.