Dalton Transactions Manuscript ID_DT-ART-03-2015-000942
REVISED Version: 17 April 2015

Copper mediated decyano decarboxylative coupling of cyanoacetate ligands: Pesci versus Lewis Acid Mechanism.

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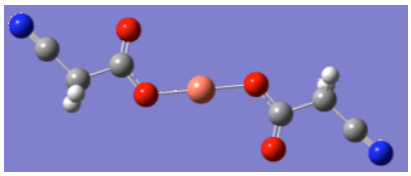
Supporting Information

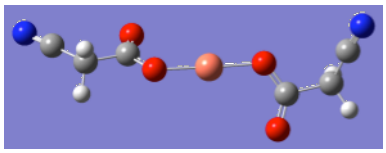
Complete citation for reference 27: Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

Supporting Information:

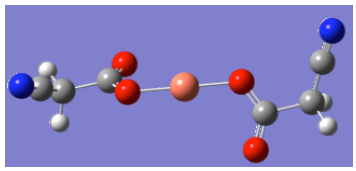
Conformers of O,O bond



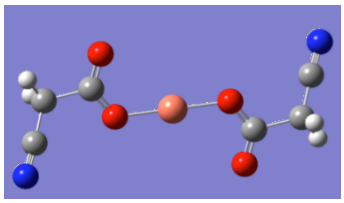
1a 0 eV (2.08eV)



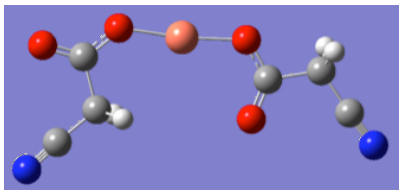
1b 0.03 eV



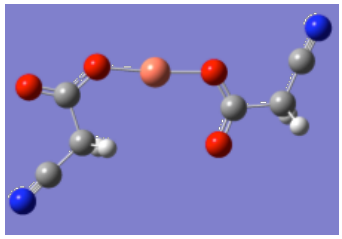
1c 0.06 eV



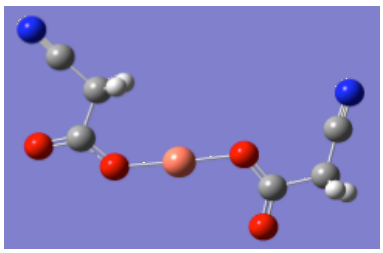
1d 0.07 eV



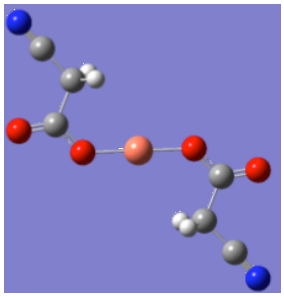
1e 0.10 eV



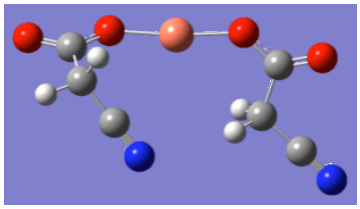
1f 0.11 eV



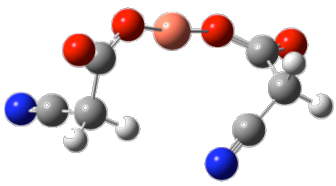
1g 0.14 eV



1h 0.24 eV

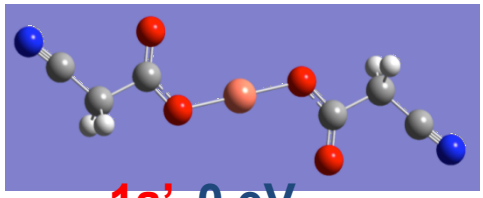


1i 0.28 eV



1j 0.33 eV

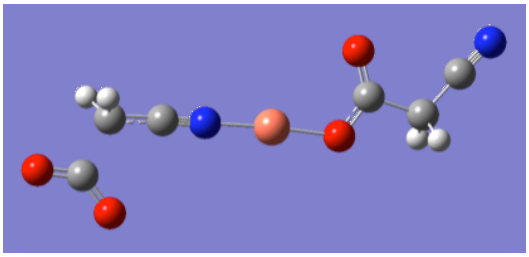
In Methanol



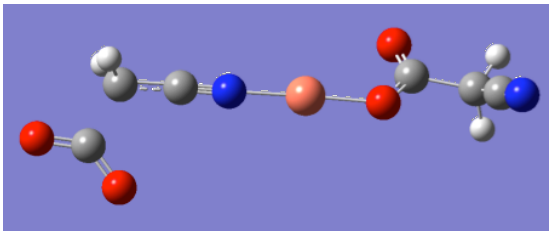
1a' 0 eV

Figure S1 DFT calculated (B3LPY/SDD6-31+G(d)) conformers of isomer **1**, $[NCCH_2CO_2CuO_2CCH_2CN]^-$ in both gas phase and methanol. Relative energies are in eV.

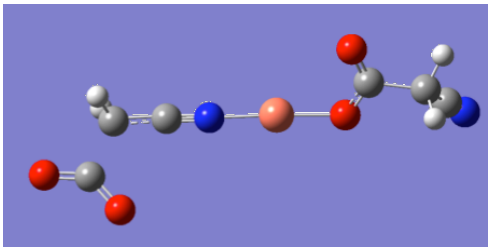
Conformers of O, N bond



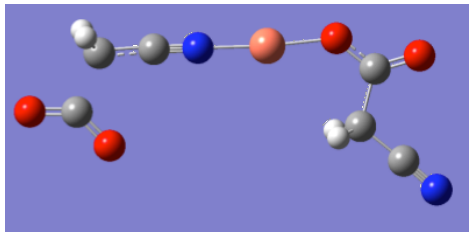
2a **0.35** eV (2.43 eV)



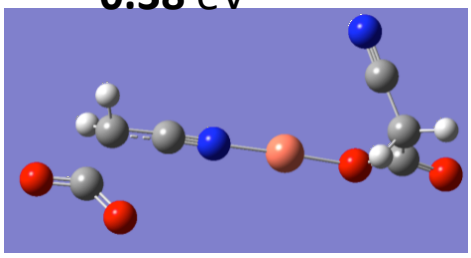
2b **0.38 eV**



2c **0.38** eV

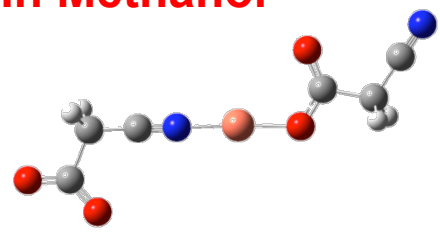


2d **0.52 eV**



2e **0.55** eV

In Methanol



2a' **0.13** eV

Figure S2 DFT calculated (B3LPY/SDD6-31+G(d)) conformers of isomer **2**, $[NCCH_2CO_2CuNCCH_2CO_2]^-$ in both gas phase and methanol. Relative energies are in eV.

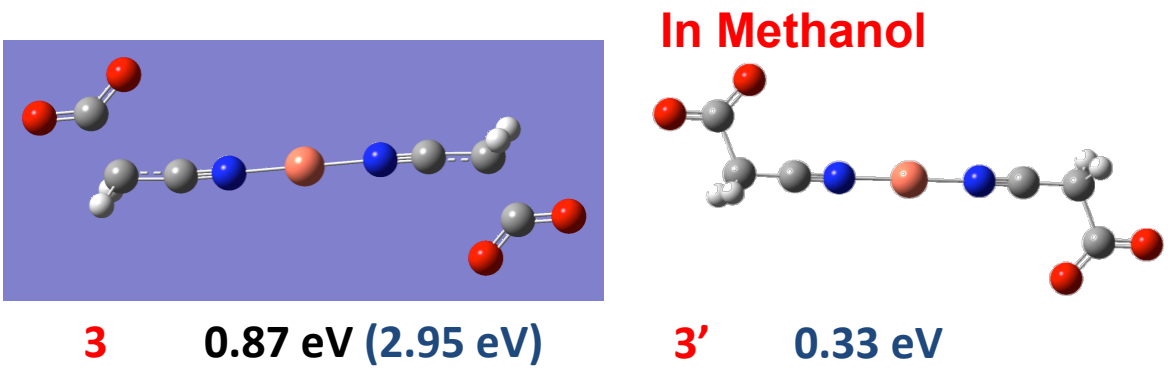
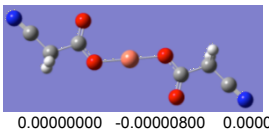


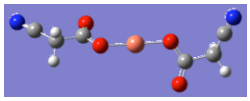
Figure S3 DFT calculated (B3LPY/SDD6-31+G(d)) isomer **3**, $[O_2CH_2CCNCuNCCH_2CO_2]^-$ in both gas phase and methanol. Relative energies are in eV.

1a



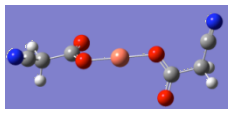
Cu	0.00000000	-0.00000800	0.00004900
O	1.73379200	0.69330400	-0.00017500
O	2.88328700	-1.27017100	-0.00013200
C	2.79273500	-0.04531100	-0.00009500
C	4.06830500	0.85305300	0.00003400
H	4.02444100	1.50865400	0.87782500
H	4.02444500	1.50884200	-0.87763100
O	-1.73379600	-0.69331100	0.00027700
O	-2.88327900	1.27017100	0.00010500
C	-2.79273500	0.04531100	0.00016100
C	-4.06831000	-0.85304500	-0.00003200
H	-4.02452500	-1.50879500	0.87766500
H	-4.02438100	-1.50868600	-0.87779100
C	5.34477700	0.13830700	-0.00001800
C	-5.34477700	-0.13829100	-0.00011600
N	6.38535100	-0.37944500	-0.00000800
N	-6.38535100	0.37946400	-0.00023400

1b



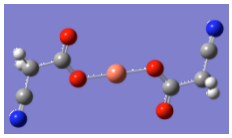
Cu	0.14093100	0.06990600	-0.21575400
O	-1.64841800	0.28657400	-0.70587500
O	-2.62689200	-0.68350800	1.10499600
C	-2.64029600	-0.11168200	0.01842600
C	-3.98766800	0.23726300	-0.68729200
H	-3.98653500	-0.23327900	-1.67768700
H	-4.01224500	1.31990100	-0.85916500
O	1.95202000	-0.20984700	0.16185400
O	2.61508100	1.96411400	0.08834300
C	2.79656700	0.75558400	0.24605300
C	4.22491200	0.28855300	0.67271900
H	4.18706700	0.06275800	1.74647500
H	4.92314800	1.11812300	0.52851000
C	-5.19909200	-0.16097500	0.02966300
C	4.73089200	-0.89271400	-0.02650400
N	-6.19255200	-0.45540800	0.55621700
N	5.18045600	-1.80882200	-0.58396000

1c



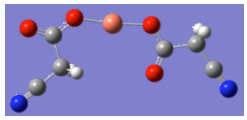
Cu	0.14093100	0.06990600	-0.21575400
O	-1.64841800	0.28657400	-0.70587500
O	-2.62689200	-0.68350800	1.10499600
C	-2.64029600	-0.11168200	0.01842600
C	-3.98766800	0.23726300	-0.68729200
H	-3.98653500	-0.23327900	-1.67768700
H	-4.01224500	1.31990100	-0.85916500
O	1.95202000	-0.20984700	0.16185400
O	2.61508100	1.96411400	0.08834300
C	2.79656700	0.75558400	0.24605300
C	4.22491200	0.28855300	0.67271900
H	4.18706700	0.06275800	1.74647500
H	4.92314800	1.11812300	0.52851000
C	-5.19909200	-0.16097500	0.02966300
C	4.73089200	-0.89271400	-0.02650400
N	-6.19255200	-0.45540800	0.55621700
N	5.18045600	-1.80882200	-0.58396000

1d



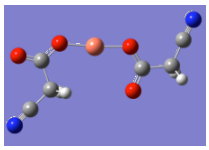
Cu	0.00000700	-0.00003800	0.00004100
O	-1.85721800	-0.08395500	0.21320900
O	-2.32440400	2.06629400	-0.36015800
C	-2.62141900	0.92937500	0.01085600
C	-4.11974300	0.66174600	0.36145800
H	-4.73203100	1.43364000	-0.11407300
H	-4.22221100	0.78136700	1.44820400
O	1.85723100	0.08384900	-0.21315300
O	2.32443600	-2.06619300	0.36096800
C	2.62144100	-0.92940100	-0.01044700
C	4.11976300	-0.66192300	-0.36116000
H	4.22229000	-0.78234600	-1.44781100
H	4.73207000	-1.43344400	0.11495300
C	-4.63654000	-0.65678600	-0.00575400
C	4.63648800	0.65690100	0.00510700
N	-5.09817100	-1.68014700	-0.30843000
N	5.09808400	1.68049700	0.30703700

1e



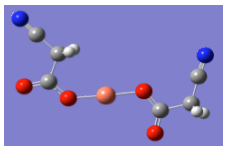
Cu	0.13550600	-1.13836100	0.00005200
O	1.96934700	-1.36545200	0.00001600
O	4.14628800	-0.82555700	-0.00039800
C	2.95587300	-0.52754600	-0.00008900
C	2.52538900	0.97439800	0.00025200
H	1.89172200	1.16218400	0.87546700
H	1.89132200	1.16247500	-0.87461300
O	-1.72775000	-1.11425400	0.00000900
O	-1.94892900	1.14781600	-0.00016500
C	-2.38449800	-0.00035100	-0.00001900
C	-3.91647500	-0.28101200	0.00018900
H	-4.15160700	-0.89448100	0.87809000
H	-4.15178400	-0.89496900	-0.87732000
C	3.63363800	1.93057800	0.00014400
C	-4.77512700	0.90344100	-0.00004600
N	4.48158200	2.72544000	0.00001500
N	-5.50354900	1.80881600	-0.00021700

1f



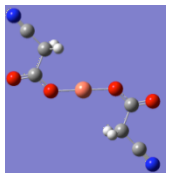
Cu	-0.10434000	-0.81490600	0.00000500
O	1.62715200	-1.46459200	-0.00006300
O	3.87029600	-1.42316500	0.00001100
C	2.77569700	-0.86824300	0.00000600
C	2.69088900	0.69249000	0.00011600
H	2.11457700	1.01695800	0.87496300
H	2.11438500	1.01710700	-0.87454800
O	-1.90396300	-0.31747700	0.00005600
O	-1.49073000	1.91541300	-0.00007700
C	-2.22772600	0.92621300	0.00000200
C	-3.75949400	1.20987700	0.00008000
H	-3.97895900	1.82900600	-0.87764200
H	-3.97889500	1.82880000	0.87796500
C	3.98358500	1.37901400	0.00002000
C	-4.65176000	0.04963900	-0.00001800
N	4.98568000	1.96790500	-0.00012000
N	-5.40488600	-0.83575700	-0.00009800

1g



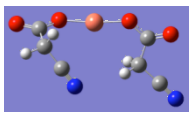
Cu	0.04237600	-0.62442000	-0.00314600
O	-1.69108200	-1.27308600	-0.03401000
O	-3.93624700	-1.25930600	-0.04804500
C	-2.84693000	-0.69493900	-0.02523900
C	-2.77949200	0.86726200	0.01986400
H	-2.20082700	1.21762200	-0.84362200
H	-2.21332500	1.16720900	0.91017200
O	1.76341100	0.09980400	0.03214900
O	2.87629500	-1.88016200	-0.01325000
C	2.80777300	-0.65049500	0.02167900
C	4.16467600	0.11448500	0.08589200
H	4.80832300	-0.28143100	-0.70736300
H	4.64195300	-0.15350300	1.03650000
C	-4.07344000	1.55127100	0.03062800
C	4.11149600	1.57311000	-0.02191000
N	-5.07636700	2.13868100	0.04310700
N	4.12371800	2.73219300	-0.10949100

1h

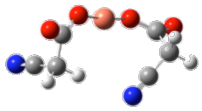


Cu	-0.00001000	-0.00001000	0.00003500
O	1.45310600	1.13330100	0.00008300
O	3.59040700	1.81419000	-0.00011900
C	2.73320700	0.93820400	0.00000700
C	3.15340800	-0.56734800	0.00014100
H	2.71255100	-1.05557200	-0.87767900
H	2.71284800	-1.05528300	0.87827400
O	-1.45311600	-1.13333900	-0.00001100
O	-3.59043300	-1.81417400	-0.00006000
C	-2.73321300	-0.93820700	-0.00000800
C	-3.15338400	0.56735200	0.00011900
H	-2.71253100	1.05556400	-0.87770900
H	-2.71280400	1.05528600	0.87824400
C	4.59750100	-0.80581100	-0.00005000
C	-4.59747300	0.80584100	-0.00005200
N	5.73450100	-1.04580400	-0.00016300
N	-5.73447000	1.04584400	-0.00015500

1i

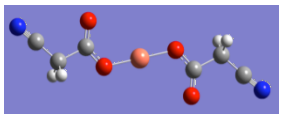


Cu	0.46536900	-0.99547200	-0.10077200
O	2.20358900	-0.74175900	-0.68516300
O	4.32340400	-0.00432400	-0.71100800
C	3.16807400	0.01364100	-0.29029700
C	2.85284100	1.02027300	0.87257200
H	3.73138900	1.65314700	1.02798000
H	2.68319000	0.43933900	1.78849600
O	-1.23171900	-1.42563200	0.47069100
O	-3.42847000	-1.23196500	0.87010200
C	-2.37702100	-0.82401700	0.38760800
C	-2.34617800	0.52195600	-0.40162900
H	-1.90874100	0.34250500	-1.39138600
H	-1.67026700	1.22170000	0.10615700
C	1.68549200	1.86953900	0.64278200
C	-3.65275300	1.15899500	-0.57403000
N	0.77663800	2.57204100	0.45942000
N	-4.66927100	1.69640200	-0.74340100



1j

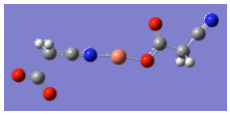
Cu	0.18585400	-0.91861200	0.02818600
O	1.90880900	-0.86699400	0.70616200
O	4.10034600	-0.39156200	0.81684500
C	2.97549600	-0.24782900	0.34081100
C	2.84297000	0.75026300	-0.86560400
H	2.65667100	0.16057600	-1.77268400
H	3.79723900	1.27099600	-0.98730800
C	1.77361900	1.73770100	-0.73272700
N	0.94652800	2.54946300	-0.63058200
N	-3.02371200	0.72789300	2.49039800
C	-2.75811100	0.85081300	1.36465800
C	-2.45566000	1.01949600	-0.05669900
H	-1.46633600	1.48236800	-0.15497500
C	-2.50641200	-0.33567000	-0.84137400
H	-3.20077300	1.69358300	-0.49061200
O	-1.50015000	-1.13140700	-0.69097100
O	-3.49246500	-0.55477800	-1.54265100



1a'

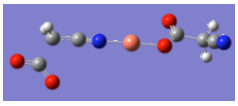
Cu	-0.00000100	-0.00005900	0.00002600
O	-1.71203900	0.74998700	-0.00001500
O	-2.84558800	-1.21146300	-0.00002700
C	-2.77673800	0.02260100	-0.00004200
C	-4.05861400	0.89221100	-0.00004600
H	-4.04358400	1.54729500	-0.87870000
H	-4.04358100	1.54731200	0.87859600
O	1.71206700	-0.75003700	0.00006400
O	2.84552900	1.21146000	0.00001100
C	2.77673700	-0.02260700	0.00006700
C	4.05865500	-0.89215900	0.00004800
H	4.04362100	-1.54728900	-0.87857200
H	4.04368700	-1.54721600	0.87872300
C	-5.29883100	0.11927300	-0.00003500
C	5.29883900	-0.11916600	-0.00002900
N	-6.29495900	-0.47877800	-0.00002600
N	6.29493600	0.47893600	-0.00009100

Figure S4 DFT calculated Cartesian coordinates for conformers of **isomer 1**



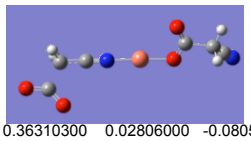
2a

Cu	-0.21932500	-0.17946300	0.00192500
O	-1.96151400	-0.82845200	0.00052600
O	-2.95542800	1.21253800	-0.00152300
C	-2.97034800	-0.01412000	-0.00097500
C	-4.30575900	-0.80945800	-0.00238900
H	-4.31372200	-1.46794500	0.87434400
H	-4.31282200	-1.46597800	-0.88062300
C	-5.52035300	0.00615500	-0.00213800
N	-6.51502600	0.60652000	-0.00189600
N	1.53485600	0.34508400	0.00333800
C	2.64705800	0.67998800	0.00417800
C	4.04012500	1.05197000	0.00415700
H	4.25674200	1.65407000	0.89290200
C	5.09465000	-0.21367500	-0.00260800
H	4.25438600	1.66336900	-0.87873500
O	4.57850900	-1.34166500	0.00317100
O	6.26653100	0.20189600	-0.01156900



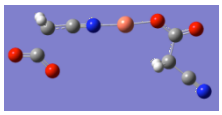
2b

Cu	-0.36321200	0.03113500	-0.07880800
O	-2.18100400	-0.27502100	0.18159300
O	-2.74238000	1.92284600	0.21402800
C	-2.99660700	0.72017300	0.27752400
C	-4.46497300	0.29968500	0.57487600
H	-5.12232300	1.14419400	0.34869300
H	-4.53502400	0.10500400	1.65328400
C	-4.93634400	-0.88733300	-0.13940800
N	-5.35680700	-1.80823900	-0.71046900
N	1.43670700	0.22819300	-0.35309600
C	2.57423300	0.37209700	-0.53894200
C	3.99370600	0.52326600	-0.74289800
H	4.27104300	1.57334500	-0.60198500
C	4.94150900	-0.37298400	0.26298200
H	4.24609600	0.24183900	-1.77064200
O	4.33652100	-1.05315600	1.10536300
O	6.14247500	-0.19921700	-0.00895500



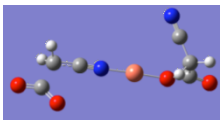
2c

Cu	0.36310300	0.02806000	-0.08056800
O	2.18082100	-0.27518300	0.18367600
O	2.73982100	1.92335200	0.21298600
C	2.99522700	0.72106600	0.27899600
C	4.46355600	0.30241300	0.57924500
H	4.53127900	0.10543700	1.65739200
H	5.12013800	1.14838200	0.35633100
C	4.93842200	-0.88230300	-0.13654300
N	5.36145000	-1.80110900	-0.70911500
N	-1.43654900	0.22145000	-0.35925100
C	-2.57398800	0.36218600	-0.54807300
C	-3.99344700	0.51134600	-0.75353600
H	-4.24690400	0.21231800	-1.77607100
C	-4.94154600	-0.36741800	0.26761900
H	-4.26969500	1.56395800	-0.63067600
O	-4.33631000	-1.04545300	1.11149700
O	-6.14288900	-0.18646000	0.00206900



2d

Cu	0.33929800	-1.00078800	-0.00087600
O	2.14924300	-1.28858000	-0.00171900
O	4.36237800	-0.93858600	-0.00186000
C	3.20720200	-0.53540000	-0.00111900
C	2.90627600	0.99559100	0.00070400
H	2.29433000	1.23528700	0.87908700
H	2.29418700	1.23734400	-0.87701300
C	4.09319200	1.85199200	0.00171800
N	5.00720600	2.56906700	0.00325200
N	-1.48072200	-0.85492000	0.00156100
C	-2.63938200	-0.76662900	0.00302600
C	-4.06856300	-0.59475900	0.00503900
H	-4.49505000	-1.06903800	0.89498200
C	-4.56939300	0.98271000	-0.00123300
H	-4.49869500	-1.07744600	-0.87859300
O	-3.66346200	1.82842600	-0.00567700
O	-5.81013500	1.03582200	-0.00018700



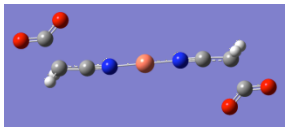
2e

Cu	-0.61959100	-0.50022800	-0.45116300
O	-2.36884800	-1.06648900	-0.40131700
O	-4.50908100	-1.28661600	0.23126300
C	-3.43088900	-0.70108800	0.23659400
C	-3.31119100	0.58909000	1.11797700
H	-2.55159500	0.41811400	1.89163600
H	-4.27217100	0.76006400	1.61161500
C	-2.94427600	1.78572600	0.36136000
N	-2.68011300	2.74592900	-0.23912300
N	1.14214200	-0.03013400	-0.56244300
C	2.25934800	0.28058700	-0.63095800
C	3.65729000	0.62405400	-0.68505700
H	3.76845400	1.70859900	-0.57703600
C	4.57991900	-0.06481200	0.49682600
H	4.06965200	0.33425700	-1.65660200
O	3.94759500	-0.59815600	1.42088600
O	5.78763200	0.10047100	0.25474600

2a'

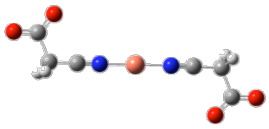
Cu	-0.22477400	-0.24317700	0.00001500
O	-1.97761000	-0.87885000	0.00058500
O	-2.92039300	1.17807900	-0.00040500
C	-2.97354800	-0.05552800	0.00018200
C	-4.32923300	-0.80066100	0.00045600
H	-4.37534300	-1.45392300	0.87942800
H	-4.37518300	-1.45484900	-0.87783600
C	-5.49109000	0.08601200	-0.00011600
N	-6.42571300	0.77601100	-0.00057200
N	1.52925900	0.29166300	-0.00007900
C	2.63287500	0.64359100	0.00007300
C	4.01967900	1.07031500	0.00030700
H	4.19550000	1.69589000	0.88268100
C	5.06118700	-0.12450100	-0.00013700
H	4.19560300	1.69664500	-0.88151300
O	4.59849500	-1.28938200	-0.00102100
O	6.25373700	0.26256400	0.00043500

Figure S5 DFT calculated Cartesian coordinates for conformers of **isomer 2**



3

Cu	-0.01838200	0.05753500	0.05353300
N	1.74463800	0.55356800	0.05300800
C	2.87163700	0.83795400	0.05139900
C	4.28147400	1.10924000	0.05660400
H	4.53993600	1.71909800	0.92786800
C	5.23362400	-0.25689400	0.09791700
H	4.55567000	1.66316600	-0.84701600
O	4.61826900	-1.33002900	0.04744300
O	6.42882200	0.06559100	0.16645400
N	-1.78138400	-0.43856100	0.05260000
C	-2.90833700	-0.72311700	0.05090600
C	-4.31815600	-0.99458700	0.05468200
H	-4.57797400	-1.60082900	0.92810700
C	-5.27070200	0.37141100	0.09060600
H	-4.59074100	-1.55242300	-0.84698400
O	-4.65491600	1.44478900	0.05219000
O	-6.46653300	0.04858800	0.14503000



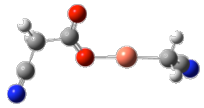
3'

Cu	-0.01842900	0.05629200	0.10845200
N	1.76958200	0.49704200	0.10783200
C	2.89555900	0.76698500	0.10566700
C	4.31123600	1.07919400	0.10096100
H	4.55387100	1.63016800	1.01655900
C	5.24433900	-0.20126700	0.00261500
H	4.52336700	1.74264900	-0.74495600
O	4.67698500	-1.31668100	-0.06029900
O	6.46547100	0.07902000	0.00045800
N	-1.80652200	-0.38411200	0.10756100
C	-2.93268200	-0.65330100	0.10517300
C	-4.34859800	-0.96433100	0.10001400
H	-4.59320300	-1.50986500	1.01832000
C	-5.28038400	0.31654300	-0.00693900
H	-4.56007400	-1.63224300	-0.74248700
O	-4.71183600	1.43107400	-0.07414500
O	-6.50173700	0.03733300	-0.01044000

Figure S6 DFT calculated Cartesian coordinates for **isomer 3**

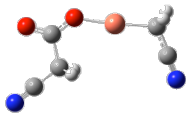
4a

Cu	1.15841900	0.12873700	0.00101900
O	-0.58785300	-0.63250200	0.00140200
C	-1.68208500	0.04419300	-0.00020900
O	-1.84726900	1.26326800	-0.00200800
C	-2.91258900	-0.92205400	0.00048700
H	-2.83340400	-1.57332900	0.87904900
H	-2.83298900	-1.57501700	-0.87678900
C	2.95672700	0.84209300	0.00094000
H	3.06931700	1.47740300	0.89060600
H	3.06814700	1.47997300	-0.88703200
C	3.98982600	-0.16722000	-0.00118000
C	-4.22661200	-0.27921400	-0.00045200
N	4.81726300	-0.99551200	-0.00289000
N	-5.29381500	0.18189500	-0.00111700



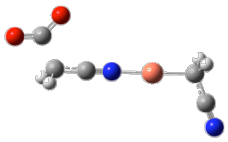
4b

Cu	-0.98850400	0.05705600	-0.25909700
O	1.54275000	1.99352400	-0.00039200
O	0.86012200	-0.17129700	0.15401300
C	1.70694700	0.78836200	0.20959400
C	3.13123700	0.33447800	0.67834800
H	3.83488100	1.15599000	0.51459000
H	3.07399800	0.14965200	1.75906700
C	-2.86215500	0.20708500	-0.71810300
H	-3.01559900	-0.26133200	-1.70046800
H	-3.09680600	1.27669900	-0.81122100
C	3.64641500	-0.87341300	0.03427900
C	-3.75491300	-0.39716100	0.24320700
N	4.10342500	-1.81085300	-0.48064000
N	-4.46885300	-0.89050900	1.02905800



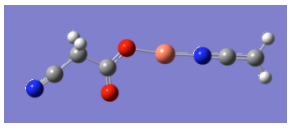
4c

Cu	-1.11661900	-0.74753000	0.01253000
O	2.90655600	-1.40884400	-0.04967200
C	1.82397800	-0.82661900	-0.02526200
O	0.65908500	-1.37659300	-0.02671700
C	1.78735900	0.73913700	0.01029700
H	1.22250200	1.05685500	0.89504800
H	1.21950900	1.09567300	-0.85765700
C	-2.98546400	-0.25921600	0.05488900
H	-3.42560200	-0.65018900	0.98286100
H	-3.48997700	-0.74715400	-0.79079200
C	-3.20655400	1.16711100	-0.01508800
C	3.09746900	1.39123800	0.02265000
N	-3.36860000	2.32463400	-0.07245300
N	4.11569500	1.95204900	0.03436100



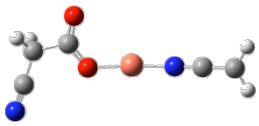
5

Cu	1.41361200	0.25528600	-0.00000700
O	-5.11714400	-0.28497900	-0.00028300
C	-3.95659100	0.16517200	-0.00002600
O	-3.47975300	1.31124800	0.00016900
C	-2.86635200	-1.06165700	0.00012000
H	-3.06337800	-1.67615000	-0.88487100
H	-3.06341100	-1.67591300	0.88526900
C	3.25107400	0.86695500	-0.00007400
H	3.40980600	1.49415700	0.88767700
H	3.40977300	1.49405900	-0.88790000
C	4.20810100	-0.21649800	-0.00003200
C	-1.48081100	-0.65370500	0.00009700
N	4.96735400	-1.10622500	0.00000400
N	-0.37376500	-0.30108900	0.00005600



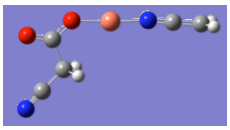
6a

O	-1.02049200	-0.16641200	0.10410900
O	-1.47235500	2.04286600	-0.18408200
C	-1.77929000	0.86231800	-0.00264900
C	-3.30244800	0.56588600	0.17668900
H	-3.85805700	1.21304200	-0.50979500
H	-3.57095800	0.87946500	1.19385900
C	-3.73383200	-0.81960600	-0.01229400
N	-4.13063200	-1.90110700	-0.16998100
Cu	0.85140500	-0.09348900	0.01958900
N	2.66115300	-0.17162300	-0.03795300
C	3.85151700	-0.21870800	-0.01875900
C	5.20658400	-0.27245200	-0.00330600
H	5.71820400	-1.22110100	0.11813300
H	5.79400500	0.63263400	-0.11303200



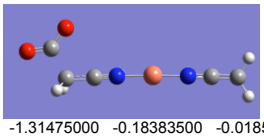
6b

Cu	-0.85085400	-0.09016700	0.02775700
O	1.02155700	-0.16606300	0.09770700
O	1.47259500	2.04574900	-0.17152300
C	1.78017000	0.86310600	-0.00525000
C	3.30531700	0.56487100	0.15256100
H	3.59343500	0.89717400	1.15824500
H	3.84974000	1.19799500	-0.55577500
C	3.73064600	-0.82478800	-0.01889400
N	4.12325400	-1.90978600	-0.16227800
N	-2.66104700	-0.16523300	-0.01220700
C	-3.85118500	-0.21932900	-0.01964200
C	-5.20603700	-0.28071900	-0.02963900
H	-5.71434200	-1.23161500	0.08796400
H	-5.79621600	0.62008200	-0.15827500



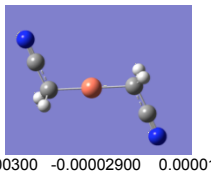
6c

Cu	-0.92152600	-0.55857200	-0.00401800
O	0.78446000	-1.28789100	-0.00244700
O	3.02696900	-1.39987200	0.00857900
C	1.96986200	-0.77591700	0.00164300
C	1.99073300	0.78921400	-0.00423100
H	1.43205600	1.15036700	0.86776000
H	1.44325200	1.14329300	-0.88616900
C	3.32411100	1.39228500	0.00157200
N	4.36068600	1.91824200	0.00580100
N	-2.61966900	0.06047000	-0.00766100
C	-3.69485200	0.57631700	0.00167000
C	-4.92150800	1.14996100	0.01093300
H	-5.45326600	1.29578600	0.94483400
H	-5.38640200	1.46912300	-0.91546100



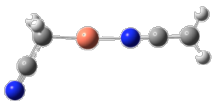
7

Cu	-1.31475000	-0.18383500	-0.01852300
C	-5.63417300	0.32940400	0.03533700
H	-6.07288100	1.29854800	0.24526100
H	-6.28679400	-0.51394200	-0.16157400
C	-4.29227500	0.17473200	0.01936700
N	-3.10687600	0.03716700	0.00499400
N	0.49834900	-0.46632200	-0.05530800
C	1.63907600	-0.68414600	-0.08735600
C	3.06096700	-0.92578300	-0.11993300
H	3.34243100	-1.30596800	-1.10775200
C	4.00373600	0.38872400	0.18489100
H	3.31690400	-1.69019600	0.62143600
O	3.39576500	1.44782600	0.40133400
O	5.20681900	0.07508400	0.14153100



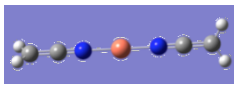
8

Cu	0.00000300	-0.00002900	0.00001300
C	1.72663800	0.95842900	0.00001400
H	1.75306900	1.60306300	-0.88997000
H	1.75308700	1.60303000	0.89002300
C	-1.72666600	-0.95842400	0.00001400
H	-1.75313700	-1.60302400	0.89002300
H	-1.75312000	-1.60305700	-0.88997000
C	2.87440600	0.08755600	-0.00001300
C	-2.87440500	-0.08751000	-0.00001300
N	-3.79142100	0.64281900	-0.00003500
N	3.79144500	-0.64274400	-0.00003500



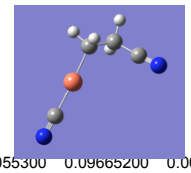
9

Cu	0.14986500	-0.28312200	0.00371200
C	-4.17750500	0.49805300	-0.00108100
H	-4.87626500	-0.31555300	-0.16418400
H	-4.56326900	1.49925400	0.15816500
C	-2.83847700	0.26753600	-0.00374400
N	-1.66421200	0.06531800	-0.00639000
C	2.03967100	-0.75145100	0.01473200
H	2.24360900	-1.34267300	0.91895000
H	2.23908700	-1.39086300	-0.85720000
C	2.93141300	0.38392600	-0.01846900
N	3.64422900	1.31260700	-0.04540400



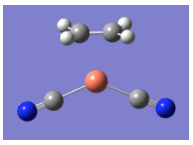
10

Cu	0.00000100	-0.00008000	-0.00005500
C	-4.36538500	0.00004200	0.00001800
H	-4.91588000	-0.65711900	0.66464200
H	-4.91583100	0.65743800	-0.66442400
C	4.36538600	0.00012500	0.00006100
H	4.91573700	0.66489200	0.65720800
H	4.91596000	-0.66462700	-0.65690100
C	-3.00867600	0.00006400	0.00005100
C	3.00867400	-0.00001200	0.00003600
N	1.81719500	0.00001300	-0.00003700
N	-1.81719600	0.00004500	0.00004900



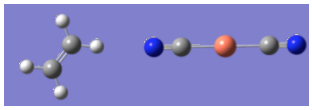
11

Cu	-0.97055300	0.09665200	0.00494600
C	0.34452700	1.52107200	0.25621000
H	-0.05265100	2.42914500	-0.23124800
H	0.44245100	1.78088600	1.32346800
C	1.77284100	1.32404500	-0.32256500
H	1.72234700	1.04158300	-1.38283400
H	2.38640700	2.24306200	-0.27984200
C	-2.32516400	-1.20914000	-0.24611400
C	2.56461600	0.29058100	0.35934200
N	3.22817200	-0.49668200	0.90263500
N	-3.17807400	-2.00089600	-0.40510100



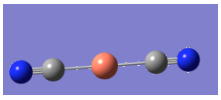
12

Cu	-0.03305000	0.06815700	0.00058400
C	0.27689700	-2.14350200	-0.00107800
C	1.50612900	-1.55180500	0.00114500
H	-0.21631200	-2.44588300	0.91882100
H	-0.21410400	-2.44311500	-0.92308700
H	2.04906700	-1.35285900	-0.91893900
H	2.04702300	-1.35558200	0.92305200
C	1.24649100	1.52997800	-0.00210700
C	-1.97367900	-0.03068500	0.00225100
N	2.05493100	2.38123600	-0.00262400
N	-3.14259500	-0.13956700	0.00076200



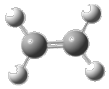
13

Cu	1.07498700	-2.73154400	-0.07399800
C	-0.56395100	4.54786500	-0.09865500
C	-1.22475100	3.43060500	0.22153200
H	-1.01854200	5.53520400	-0.02214800
H	0.46507300	4.51470600	-0.45210600
H	-0.77519100	2.44095700	0.14693900
H	-2.25512100	3.47441300	0.57456600
C	1.68439500	-4.51307900	-0.14128300
C	0.46482000	-0.95027400	-0.00647400
N	0.08467700	0.15816900	0.03563900
N	2.06359800	-5.62216900	-0.18310700



14

Cu	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.88493300
C	0.00000000	0.00000000	-1.88493300
N	0.00000000	0.00000000	-3.05802200
N	0.00000000	0.00000000	3.05802200

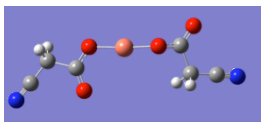


CH2CH2

C	-0.00001800	-0.66769000	0.00000000
C	-0.00001800	0.66769000	0.00000000
H	0.00005500	-1.24028000	0.92508000
H	0.00005500	-1.24028000	-0.92508000
H	0.00005500	1.24028000	-0.92508000
H	0.00005500	1.24028000	0.92508000

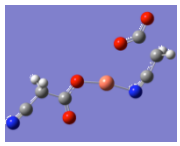
CO2

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16976200
O	0.00000000	0.00000000	-1.16976200



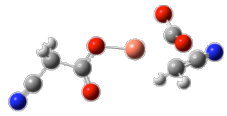
TS1a-1e

Cu	0.02456000	-0.85286000	-0.17717900
O	-1.79025800	-0.91579300	0.24204500
O	-2.32717900	1.17981300	-0.45994700
C	-2.58462600	0.07997300	0.02105300
C	-4.03165500	-0.28103900	0.47369700
H	-4.00646000	-0.49917000	1.54820000
H	-4.32620500	-1.21244700	-0.02378600
O	1.81691500	-0.93186400	-0.61126400
O	3.65205300	-1.17351500	0.69017900
C	2.89748700	-0.52643600	-0.02641500
C	3.22619100	0.96108200	-0.38248800
H	2.41714000	1.59149300	0.00611300
H	3.19978900	1.06509700	-1.47342400
C	-5.04613000	0.74131500	0.21709800
C	4.50656200	1.46165000	0.11783000
N	-5.89151500	1.51722800	0.03325600
N	5.51784000	1.89699800	0.49078900



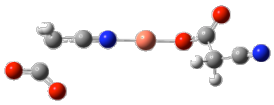
TS1e-2a

Cu	0.34064900	-0.49020300	0.00111000
O	-1.26000200	0.52184800	0.00240200
O	-2.72155400	-1.22149100	-0.00307600
C	-2.42534900	-0.02804000	0.00012900
C	-3.53476300	1.07043100	0.00203500
H	-3.38017000	1.71204800	-0.87346800
H	-3.38188300	1.70724500	0.88134200
O	4.45871500	1.80780200	-0.00177700
O	2.24275600	1.25634200	-0.00030600
C	3.47226300	1.05737800	-0.00099800
C	3.95136100	-0.52951600	-0.00088400
H	4.56770800	-0.68702900	0.88895600
H	4.56668200	-0.68747600	-0.89135400
C	-4.91263400	0.57894400	-0.00064100
C	2.79418100	-1.37894800	-0.00000100
N	-6.02464500	0.24035100	-0.00266100
N	1.72738400	-1.86412100	0.00074100



TS1e-4a

Cu	-0.52517200	-0.25471900	-0.13383500
O	1.27312300	-0.67159000	-0.57397900
C	2.23071700	0.00312000	-0.02974300
O	2.15484300	0.92741400	0.77709100
C	3.61117900	-0.50669700	-0.53957400
H	3.63203300	-0.39771500	-1.63052700
H	3.67583900	-1.58199100	-0.33572200
O	-3.27957600	-1.45454500	1.23218000
C	-2.70119000	-1.04578800	0.25709700
O	-2.38585700	-1.34417900	-0.88993600
C	-2.19241400	0.87899900	0.68723300
H	-1.19709000	1.38290400	0.70044200
H	-2.53189600	0.83772800	1.72131300
C	-3.07589100	1.66318800	-0.13735200
C	4.78123400	0.16112900	0.03088100
N	-3.79624300	2.28072500	-0.81792200
N	5.74325000	0.65719600	0.45386700

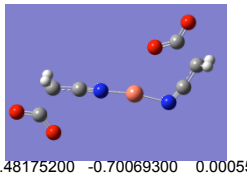


TS2a-2d

Cu	-0.24274300	-0.66968600	-0.21892600
O	-2.00109400	-0.78796000	-0.70546100
O	-3.95316900	-1.31526600	0.29686000
C	-3.15232500	-0.51750400	-0.16843900
C	-3.48712000	1.00549200	-0.23044000
H	-3.39866000	1.33117000	-1.27372300
H	-2.72034600	1.55459100	0.32943600
C	-4.80747800	1.37579000	0.27962700
N	-5.84744800	1.71298800	0.67321600
N	1.52732900	-0.59832300	0.21931700
C	2.65613600	-0.54481900	0.48951200
C	4.06327900	-0.44155100	0.77836200
H	4.55567900	-1.39420500	0.55881500
C	4.84902300	0.74637800	-0.05989400
H	4.20273700	-0.22277900	1.84256000
O	4.11929400	1.50846500	-0.71144000
O	6.07395300	0.67060400	0.13400000

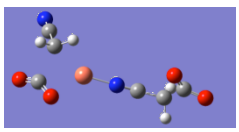
TS2d-2e

Cu	-0.44265200	-0.79330200	-0.23284400
O	-2.20166000	-1.22785700	0.06157900
O	-4.36818400	-1.08161600	0.61821900
C	-3.25553400	-0.59219400	0.46181600
C	-3.07864800	0.93096400	0.79166200
H	-2.02201200	1.21287500	0.84533300
H	-3.53359100	1.11070700	1.77242300
C	-3.74366100	1.78965200	-0.18829400
N	-4.25513600	2.48469300	-0.96728800
N	1.32337800	-0.46430600	-0.55738300
C	2.44939100	-0.25179800	-0.75009300
C	3.85271200	0.01668700	-0.92561000
H	3.98358800	0.81079300	-1.66852100
C	4.63056400	0.51413000	0.44738300
H	4.35752300	-0.88220700	-1.29326000
O	3.89611100	0.74998500	1.41762000
O	5.85432900	0.58026800	0.24608700



TS2e-3

Cu	0.48175200	-0.70069300	0.00055200
O	-4.42434800	-1.09472300	0.00173200
O	-5.87060200	0.67684600	-0.00619200
C	-4.77006100	0.09748000	-0.00122400
C	-3.54455400	1.19362400	0.00306200
H	-3.66669100	1.82375800	0.89039400
H	-3.66472200	1.82980500	-0.88017900
O	2.46425900	1.28414900	0.00033300
O	4.66625000	1.90118100	-0.00070100
C	3.69686200	1.13470600	-0.00046300
C	4.23558000	-0.46007300	-0.00147500
H	4.85286500	-0.59535700	0.89059500
H	4.85180300	-0.59458800	-0.89439600
C	-2.22195600	0.61838300	0.00266700
C	3.09767600	-1.32418900	-0.00116900
N	-1.17394900	0.11877000	0.00185700
N	2.03254300	-1.81058800	-0.00074200

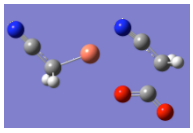


TS2e-5

Cu	-0.76695400	-0.25131700	0.07358600
N	1.00650500	-0.14027900	-0.45485100
C	2.12831000	-0.06322900	-0.74765200
C	3.53319200	0.02731800	-1.05401900
H	3.71463800	0.90761900	-1.68003300
C	4.51157200	0.17232600	0.26769600
H	3.84769700	-0.85980500	-1.61270700
O	3.92645700	0.34155900	1.34807800
O	5.70543100	0.10028200	-0.06965100
O	-4.00893700	-0.99026800	-0.60032300
C	-2.98087600	-1.13628800	-0.00627100
O	-2.13944100	-1.95917300	0.34677400
C	-2.57472400	0.65541800	0.88677400
H	-1.67131500	0.97648600	1.44786500
H	-3.28637300	0.35306800	1.66016900
C	-3.08785900	1.75763100	0.11449800
N	-3.49347100	2.63922000	-0.53293100

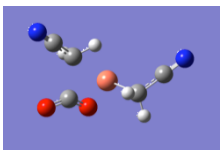
TS4a-4c

Cu	1.16630800	-0.53652100	-0.05632700
O	-0.60014100	-0.75607700	-0.67088000
C	-1.78293200	-0.63146100	-0.17791200
O	-2.49721200	-1.49871900	0.31754300
C	-2.31414400	0.83797000	-0.31437400
H	-2.21010900	1.14139200	-1.36264700
H	-1.65035700	1.49236500	0.26355300
C	2.99163800	-0.36888100	0.55092600
H	3.56648000	-1.21600700	0.15123200
H	2.99841200	-0.44299900	1.64720700
C	3.62262800	0.86819600	0.15096500
C	-3.69525900	1.05785500	0.11434700
N	4.12169800	1.87375600	-0.17995100
N	-4.79028400	1.27491000	0.43953800



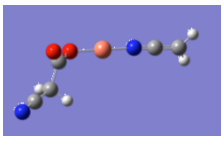
TS4c-5

Cu	-0.72515900	0.17782700	0.00004800
O	3.71769900	-1.31286800	-0.00004700
C	2.61796600	-0.73802900	-0.00003200
O	1.44051300	-1.15502000	-0.00001700
C	2.79566100	0.89067100	-0.00003600
H	3.37340900	1.16440900	-0.88830400
H	3.37345400	1.16441000	0.88820200
C	-2.25358700	-1.03869800	0.00009300
H	-2.14840200	-1.67434700	0.88912700
H	-2.14829900	-1.67452900	-0.88879800
C	-3.54696300	-0.40310000	-0.00004500
C	1.50772200	1.53781900	-0.00000400
N	-4.59276300	0.12489500	-0.00015800
N	0.39118600	1.89141700	0.00002300



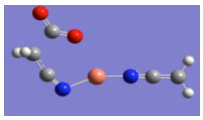
TS4c-8

Cu	0.41510200	-0.13825100	0.05859000
O	-2.42765400	-1.03578500	0.92362100
C	-1.70094800	-1.17326900	-0.03861600
O	-1.18511700	-2.04477200	-0.73228900
C	-1.44018800	0.51719900	-0.91932100
H	-0.53114300	0.73852000	-1.51615400
H	-2.18305600	0.21570800	-1.66334800
C	2.16382000	-0.25620000	0.89903800
H	2.13652600	0.32419800	1.82998600
H	2.33307600	-1.31089200	1.15211500
C	-1.88724500	1.69120000	-0.20817200
C	3.23571000	0.22157600	0.05810100
N	4.09345600	0.61156700	-0.63582100
N	-2.25318300	2.62888300	0.38174500



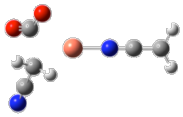
TS6a-6c

Cu	-1.02765400	-0.34415400	-0.21583700
O	0.73411700	-0.80709200	-0.54488500
O	2.45265700	-1.36062200	0.82023800
C	1.87316800	-0.62099700	0.03317300
C	2.54233900	0.71688200	-0.43097900
H	1.90204700	1.54483700	-0.10272800
H	2.53964300	0.73849900	-1.52694400
C	3.90450800	0.94604900	0.05036000
N	4.99011300	1.16557000	0.40359800
N	-2.76206500	0.10701300	0.01539600
C	-3.88459400	0.45786700	0.21034100
C	-5.16330600	0.85113200	0.42472400
H	-5.78900700	0.32387800	1.13657400
H	-5.57395500	1.70129300	-0.10911200



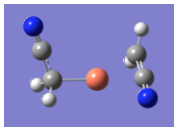
TS6c-7

O	-1.25622500	1.22483900	-0.00003600
O	-3.45579900	1.84226500	0.00000400
C	-2.49048200	1.06441100	-0.00000100
C	-3.01516400	-0.50965100	0.00005500
H	-3.63427700	-0.65109400	-0.89055400
H	-3.63421600	-0.65105100	0.89071200
C	-1.87673200	-1.38310000	0.00003800
N	-0.81792900	-1.88398100	0.00001600
Cu	0.64110300	-0.56622000	-0.00002700
N	2.35138200	0.08795200	-0.00006500
C	3.47548900	0.48333900	0.00000500
C	4.75528600	0.93289600	0.00007400
H	5.58434100	0.23330100	0.00011600
H	4.96381100	1.99722400	0.00009500



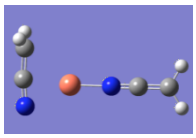
TS6c-9

O	-2.45141400	-1.07621900	1.15572600
C	-1.67992100	-1.21520600	0.24050900
O	-1.00665300	-2.05785400	-0.35020700
C	-1.67531100	0.45238700	-0.83159900
H	-0.89199500	0.76697600	-1.55280400
H	-2.45614000	0.00209000	-1.45119200
C	-2.18545700	1.59814900	-0.12203700
N	-2.59663100	2.52231400	0.45941400
Cu	0.33324700	-0.14403600	-0.22336600
N	2.12645700	0.09683600	0.01163400
C	3.29743100	0.25407700	0.17372500
C	4.62792600	0.43292300	0.35037200
H	5.28247900	-0.41939700	0.49647300
H	5.04925800	1.43193900	0.37782800



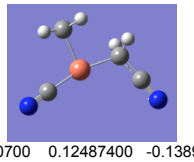
TS9-8

Cu	-0.21876800	-0.28751200	0.10989300
C	-2.13999100	1.42773000	0.33006500
H	-2.47853000	1.56890600	1.35108100
H	-1.97146400	2.30368600	-0.28699300
C	1.64107500	-0.65464500	0.58359300
H	1.85855500	-1.70478600	0.34619600
H	1.73895600	-0.51993900	1.66972200
C	-2.24393400	0.18613400	-0.25827300
C	2.59500800	0.19329900	-0.08871500
N	3.36368800	0.88330300	-0.64151300
N	-2.20885800	-0.91546600	-0.73947400



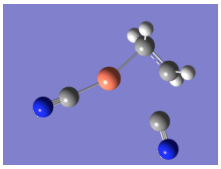
TS10-9

Cu	0.33937500	-0.13740300	-0.00001300
C	-4.02915200	0.16982000	0.00003500
H	-4.50683100	1.14400500	0.00001000
H	-4.65040700	-0.71965300	0.00010200
C	-2.67421700	0.06575300	-0.00000500
N	-1.48656900	-0.02511300	-0.00004600
C	2.44345300	1.31008200	0.00001500
H	2.59344600	1.84273900	-0.93287800
H	2.59340100	1.84274600	0.93291000
C	2.40536200	-0.06752900	0.00002100
N	2.23740200	-1.25973000	0.00002400



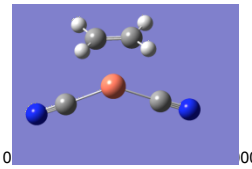
TS8-11

Cu	-0.31860700	0.12487400	-0.13892500
C	-1.19649000	1.89963400	0.09630800
H	-0.68358300	2.31603000	0.99433000
H	-2.24244300	1.75493200	0.43385700
C	1.57812800	0.75059600	-0.05818900
H	1.73839500	1.29545100	-0.99554300
H	1.65388300	1.45481400	0.77726500
C	-1.93467000	-0.87473300	0.01420700
C	2.54144600	-0.30909100	0.08835700
N	3.29694600	-1.19746100	0.20106500
N	-2.90765400	-1.52340900	0.09531700



TS11-12

Cu	-0.46821700	-0.39967000	-0.00000100
C	1.04996600	-1.75909100	-0.00000100
C	2.05628200	-0.76574700	0.00000300
H	0.87494800	-2.31234700	0.92312500
H	0.87495300	-2.31234600	-0.92312900
H	2.62033300	-0.58403300	-0.90932900
H	2.62032600	-0.58403200	0.90933900
C	1.64325600	1.27650300	0.00000000
C	-2.16836300	0.39058600	0.00000000
N	1.98921400	2.39914300	-0.00000100
N	-3.26051800	0.81938200	0.00000100



TS12-13

Cu	0		001200
C	0.68123600	2.00975300	0.00025400
C	-0.68124100	2.00975100	0.00007100
H	1.25538200	2.06195900	0.92140000
H	1.25562800	2.06210900	-0.92072900
H	-1.25538500	2.06210700	-0.92106600
H	-1.25563200	2.06195600	0.92106400
C	1.79672300	-0.87319600	0.00018100
C	-1.79672100	-0.87319800	-0.00032200
N	-2.89917800	-1.27680400	-0.00050800
N	2.89918000	-1.27680100	0.00030500

Figure S7 DFT calculated Cartesian coordinates for all structures appeared in this report.