Electronic Supplementary Information

Direct reduction of NO into N_2 catalyzed by fullerene-supported rhodium clusters

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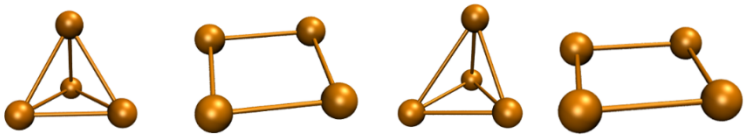
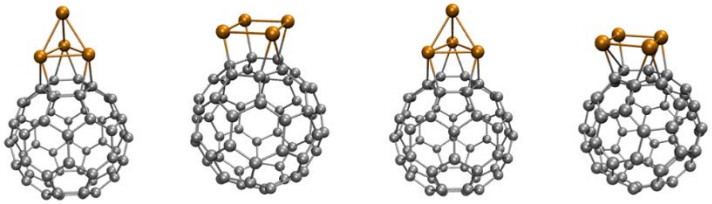
Confirmation of the ground state structures of Rh_4^+, $C_{60}Rh_4^+$, and $C_{60}Rh^+$

Figures S1, S2, and S3 respectively show the energy differences between the isomers of Rh_4^+, $C_{60}Rh_4^+$, and $C_{60}Rh^+$. Calculations show that for Rh_4^+ the pyramidal structure is more stable than the square structure, with the doublet states being slightly more stable than the quartet states. For $C_{60}Rh_4^+$, the structure with a square Rh_4^+ moiety possessing a quartet state is most stable and its simulated infrared spectrum gives the largest cosine similarity score (see Figure S4). For $C_{60}Rh^+$, the $\eta^{6\text{-}6}$ structure with a triplet state is the most stable one, consistent with previous results.[1]



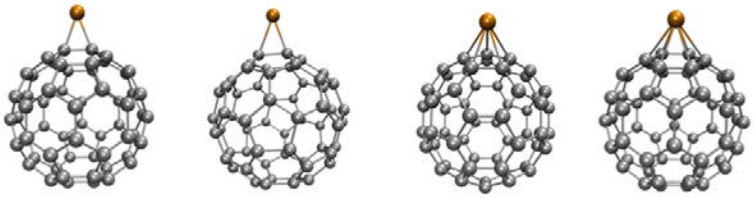
Iso1 (doublet)	Iso2 (doublet)	Iso1 (quartet)	Iso2 (quartet)
0.00 (BPW91)	0.38	0.07	0.30
0.00 (PBE)	0.39	0.07	0.26
0.14 (B3LYP)	1.97	0.00	1.18

Figure S1. Energy differences (in eV) between different isomers of Rh_4^+ at the BPW91, PBE, and B3LYP levels.



Iso1 (doublet)	Iso2 (doublet)	Iso1 (quartet)	Iso2 (quartet)
0.25 (BPW91)	0.14	0.16	0.00
0.26 (PBE)	0.14	0.17	0.00
0.28 (B3LYP)	0.00	0.04	0.04

Figure S2. Energy differences (in eV) between different isomers of $C_{60}Rh_4^+$ at the BPW91, PBE, and B3LYP levels.



$\eta^{2(6\text{-}6)}$, 0.00 $\eta^{2(5\text{-}6)}$, 0.25 η^5, 0.36 η^6, 0.45

Figure S3. Energy differences (in eV) between different isomers of $C_{60}Rh^+$ at the BPW91 level.

Cosine Similarity Score

Cosine similarity score was employed to quantitatively evaluate the agreement between calculated and experimental infrared spectra.[2-5] Figure S4 displays the calculated cosine similarity scores of the theoretical spectra and experimental one for $C_{60}Rh_4^+$. It can be seen that the cosine similarity score for the Iso2 quartet is largest, suggesting Iso2 $C_{60}Rh_4^+$ with a quartet state the most probable structure exist in the experiment.

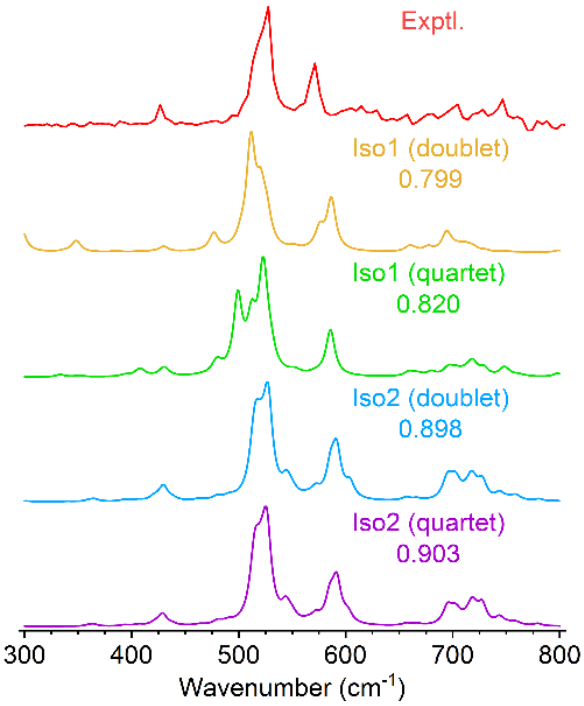


Figure S4. The theoretical infrared spectra for the four isomers of $C_{60}Rh_4^+$ and their comparison with experimental spectrum. Cosine similarity scores are provided.

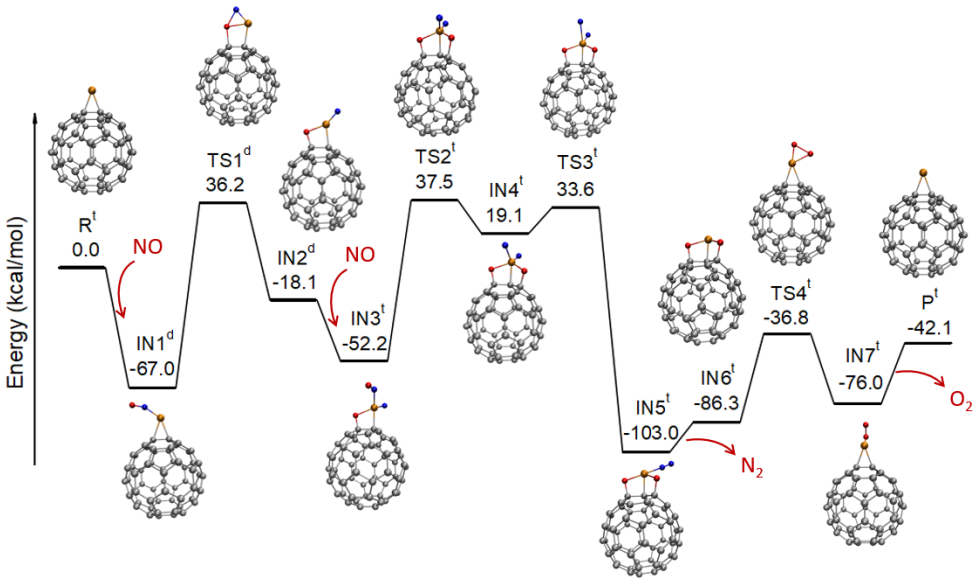


Figure S5. Reaction pathway of NO reduction on $C_{60}Rh^+$ calculated at the BPW91/6-31G(d)&SDD level of theory. R represents for reactants, IN for intermediates, TS for transition states, and P for products. All energies are provided relative to the energies of the reactants, i.e., $C_{60}Rh^+$ and two NO molecules. Calculations show that N–O dissociations post high energy barriers of 103.2 (TS1) and 89.7 (TS2) kcal/mol, respectively.

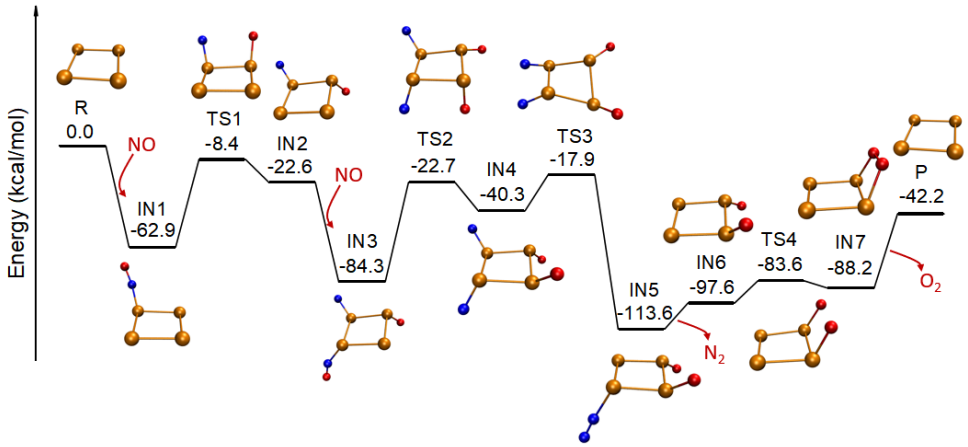


Figure S6. Reaction pathway of NO reduction on square Rh_4^+ calculated at the BPW91/6-31G(d)&SDD level of theory. R represents for reactants, IN for intermediates, TS for transition states, and P for products. All energies are provided relative to the energies of the reactants, i.e., Rh_4^+ and two NO molecules.

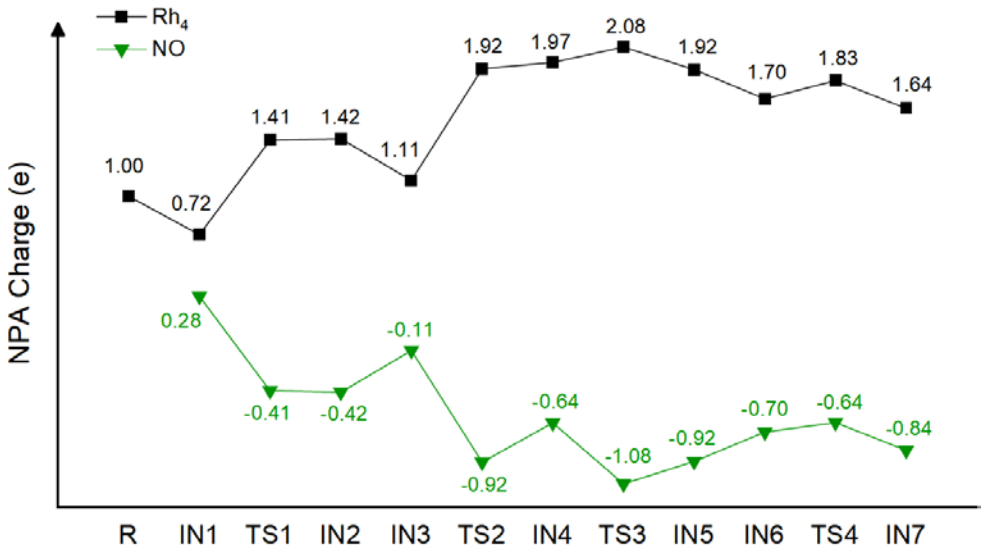


Figure S7. Calculated NBO partial charges (*e*) of pyramid Rh_4^+ cluster (black square) of NO reduction catalyzed by Rh_4^+

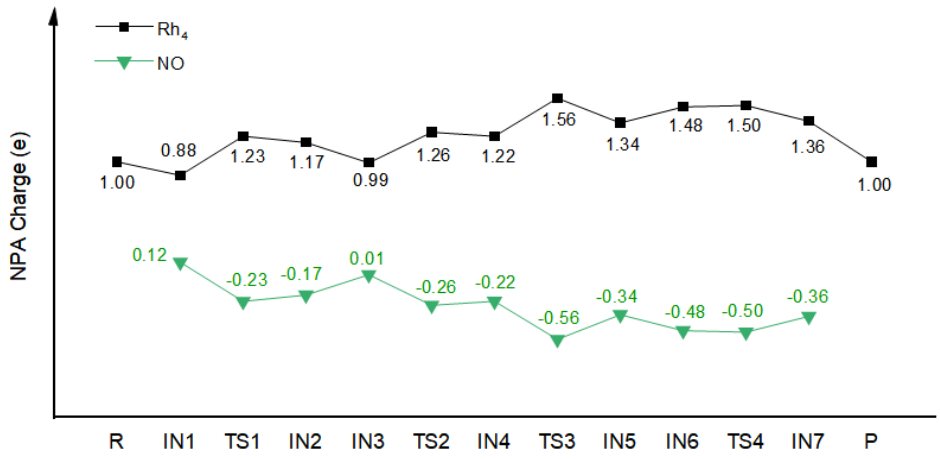


Figure S8. Calculated NBO partial charges (*e*) of square Rh_4^+ cluster (black square) of NO reduction catalyzed by Rh_4^+

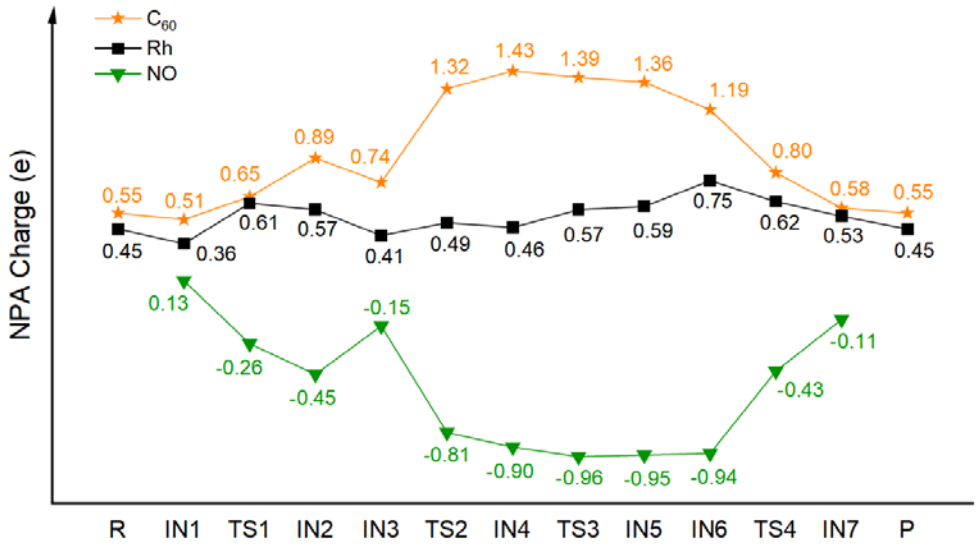


Figure S9. Calculated NBO partial charges (*e*) of Rh^+ (black square) and C_{60} (orange star) of NO reduction catalyzed by $C_{60}Rh^+$

Cartesian coordinates of the most stable $C_{60}Rh_4^+$, $C_{60}Rh^+$, and Rh_4^+ at the BPW91/6-31G(d)&SDD level of theory

$C_{60}Rh_4^+$			
C	8.5931280	6.7238380	7.5364780
C	9.4582700	6.3148530	6.4189110
C	7.6709300	5.7625170	8.1271720
C	9.4215980	4.9973880	5.9426630
C	9.5093960	4.7352090	4.5172900
C	9.5499350	7.4220430	5.4823380
C	9.6425580	7.1739790	4.1007210
C	9.6196220	5.8052170	3.6088130
C	5.7909210	7.5697550	8.2658840
C	6.7707700	8.5068530	7.5719080
C	6.2584510	6.1412450	8.5552880
C	8.1379890	8.1144760	7.2558410
C	8.7359940	8.5205190	5.9741390
C	6.0179650	9.2887850	6.5752740
C	6.6254480	9.6984810	5.3796710
C	8.0074400	9.3094750	5.0732810
C	4.1458960	5.2608700	7.4880580
C	3.6945830	6.6399060	7.2092580
C	5.3987670	5.0272240	8.0625690
C	4.5127330	7.7309570	7.5163260
C	4.6460890	8.8174830	6.5635910
C	2.9462430	6.6170390	5.9681970
C	3.0396650	7.6903380	5.0592540
C	3.9066050	8.8129520	5.3638820
C	5.7733260	3.1234480	6.5109520
C	4.4620310	3.3530230	5.9335860
C	6.2384240	3.9631920	7.5434330
C	3.6684530	4.4150260	6.4118360
C	2.9255780	5.2465090	5.4736790
C	4.5480680	3.0961350	4.5044910
C	3.8332220	3.9015700	3.6014490
C	3.0034160	4.9943910	4.0963770
C	8.4864770	4.0261300	6.5232510
C	8.0109330	3.1702840	5.4512760
C	7.6209670	4.4024890	7.5606810
C	6.6760010	2.7249400	5.4439950
C	5.9206730	2.7046210	4.2004330
C	8.6395440	3.6071970	4.2105250
C	7.9098930	3.5903750	3.0128560
C	6.5250560	3.1325130	3.0070840
C	4.0139730	5.7026320	2.0915070
C	4.4592200	4.3422500	2.3648160
C	5.7832380	3.9646580	2.0719980
C	4.9071860	6.6367740	1.5347490
C	4.0527750	8.3973480	3.0533370
C	3.1271430	7.4284570	3.6314430
C	3.1114160	6.1055890	3.1577710
C	4.9263140	8.0062730	2.0253270
C	6.7767260	9.2855940	3.0655990
C	5.8733570	9.6850240	4.1380050
C	4.5345850	9.2510000	4.1286330
C	6.3123030	8.4607000	2.0303800
C	8.4171530	7.1494480	2.0918030
C	8.8985090	8.0038510	3.1659640
C	8.0932470	9.0539310	3.6464920
C	7.1462980	7.3712500	1.5357840
C	6.7064930	4.9323730	1.4959050
C	8.0217830	4.7009170	2.0744670
C	8.8631890	5.7870760	2.3669930
C	6.2764040	6.2448440	1.2302910
Rh	5.8390550	8.4378690	10.1048570
Rh	8.8743760	6.6334690	9.6459080
Rh	8.0705250	9.0842430	9.1508800
Rh	6.5818390	6.1751120	10.5638460

$C_{60}Rh^+$			
C	2.1089020	-2.2498480	-1.7938820
C	1.2936900	-1.7040880	-2.8645880
C	1.5306790	-3.1045930	-0.8334570
C	-0.0736710	-2.0290860	-2.9412830
C	-1.0468060	-1.0016560	-3.2677620
C	1.7343240	-0.3355590	-3.1147160
C	0.7935160	0.6573180	-3.4285360
C	-0.6222170	0.3191680	-3.5029720
C	2.8005500	-1.9815320	0.9633160
C	3.3902040	-1.0904080	-0.0216480
C	1.8781760	-2.9609770	0.5663220
C	3.0568370	-1.2249490	-1.3801770
C	2.8252750	-0.0395980	-2.1958290
C	3.5031190	0.2363400	0.5714810
C	3.2784060	1.3783010	-0.2151970
C	2.9346670	1.2382860	-1.6242060
C	0.4109740	-2.4768940	2.5271650
C	1.3854870	-1.4768630	3.0151700
C	0.6658770	-3.2127410	1.3603970
C	2.6021020	-1.2240370	2.2186540
C	2.9850160	0.1752160	1.9279470
C	0.5955320	-0.3205580	3.4933450
C	1.0251710	0.9914180	3.2421870
C	2.2369800	1.2424090	2.4473640
C	-1.7180280	-3.0432630	0.7126580
C	-1.9792860	-2.2689850	1.9175710
C	-0.4151820	-3.5080950	0.4412940
C	-0.9277800	-1.9852910	2.8049620
C	-0.8141890	-0.6587800	3.3987490
C	-2.9563950	-1.2384430	1.5907750
C	-2.8470230	0.0394270	2.1624040
C	-1.7558090	0.3344050	3.0823560
C	-0.6721620	-2.9159070	-1.9496360
C	-2.0185940	-2.4317050	-1.6670950
C	0.1143590	-3.4420150	-0.9156060
C	-2.5321840	-2.4970520	-0.3584160
C	-3.2990930	-1.3792340	0.1823070
C	-2.2492840	-1.2506720	-2.4792130
C	-2.9837820	-0.1705900	-1.9560370
C	-3.5218610	-0.2373010	-0.6026550
C	-2.1267230	2.2499100	1.7662820
C	-3.0775030	1.2247200	1.3476100
C	-3.4092500	1.0887880	-0.0098450
C	-1.5450930	3.1036880	0.8102490
C	0.6581630	2.9072740	1.9255780
C	0.0579010	2.0205330	2.9153830
C	-1.3123050	1.6988090	2.8348790
C	-0.1278080	3.4392770	0.8941820
C	1.6999560	3.0433300	-0.7400670
C	2.5138970	2.4918670	0.3284670
C	2.0035030	2.4233300	1.6406410
C	0.4000330	3.5070000	-0.4639500
C	-0.4387310	2.4609330	-2.5439500
C	0.9072190	1.9833030	-2.8354140
C	1.9579580	2.2686390	-1.9496900
C	-0.6864930	3.2133110	-1.3812530
C	-2.8013840	1.9715480	-0.9982620
C	-2.5431610	1.1944870	-2.2015440
C	-1.3829340	1.4351390	-2.9610060
C	-1.8895240	2.9635890	-0.5933490
Rh	3.0854410	-2.0816780	4.0530090

Rh_4^+			
Rh	0.2128110	1.2404850	5.4326590
Rh	2.4844410	0.5876130	4.9540880
Rh	1.7865360	2.9451640	4.4989710
Rh	2.0651730	2.2369160	6.7864860

References

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