Supporting Information

Dioxygen Adducts of Rhodium *N*-Heterocyclic Carbene Complexes†

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Table S1 Crystallographic data for Rh^{I} complexes: RhCl(IPr)(PPh$_3$)(O$_2$) (**2**), *trans*-RhCl(IMes)$_2$(O$_2$) (**3**),[1] *trans*-RhCl(IPr)$_2$(O$_2$) (**4**),[1] and repeat determinations of **3** and **4**.

Complex	**2**	**3 and 3′**[a1]	**4, 4′,4″**[a1]
	2: ccdc888671	**3:** ccdc915322 **3′:** ccdc725326	**4:** ccdc915321 **4′**: ccdc888672 **4″**: ccdc725327
Empirical formula	$C_{45}H_{51}N_2O_2PClRh$	**3**:$C_{44}H_{52}N_4O_{2.5}RhCl$ **3′**:$C_{43.46}H_{50.91}ClN_4O_{2.36}Rh$	$C_{54}H_{72}N_4O_2ClRh$
Fw	821.21	815.26/806.46	947.52
Cryst colour, habit	blue, needle	blue, plate	blue, needle
Cryst size, (mm)	0.10 x 0.10 x 0.40	**3**:0.03 x 0.20 x 0.30 **3′**:0.35 x 0.08 x 0.08	**4**:0.05 x 0.10 x 0.40 **4′**:0.12 x 0.16 x 0.60 **4″**:0.40 x 0.20 x 0.04
Crystal system	hexagonal	monoclinic	monoclinic
Space group	$P6_1$	C2/c	$P2_1/c$
a (Å)	25.697(1)	**3**: 32.900(16) **3′**: 33.058(4)	**4**:12.6048(5) **4′**:12.6052(11) **4″**:12.6388(12)
b (Å)	25.967	**3**:10.8535(9) **3′**:10.8530(12)	**4**:21.1023(10) **4′**:21.171(2) **4″**:21.168(2)
c (Å)	12.2498(5)	**3**:23.717(2) **3′**:23.786(3)	**4**:19.8279(9) **4′**:19.8672(18) **4″**:19.895(2)
α, β, γ (deg)	90, 90, 120	**3**:90, 100.445(3), 90 **3′**:90, 100.712(2),90	**4**:90, 95.063(1), 90 **4′**:90, 95.098(5), 90 **4″**:90, 95.120(2), 90
V (Å^3)	7005.3(4)	**3**:8328.4(12) **3′**:8385.2(16)	**4**:5253.5(4) **4′**:5280.9(8) **4″**:5301.3(9)
Z	6	8	4

μ (mm^{-1})	0.491	**3**:0.515 **3′**:0.511	**4**:0.417 **4′**:0.415 **4″**:0.417
Total no. of rflns	44176	**3**:33986; **3′**:23948	**4**:40534 **4′**:61476 **4″**:30576
No. of unique rflns	8170	**3**:7617; **3′**:7376	**4**:9294 ; **4′**:12543 **4″:**9330;
No. of variables	488	**3**:512; **3′**:490	**4**:588; **4′**:601 **4″**596
*R*1 (*I* >2σ(I))	0.038	**3**:0.044; **3′**:0.0432	**4**:0.049; **4′**:0.040 **4″**:0.0384;
wR2 (all data)	0.076	**3**:0.098; **3′**:0.1013	**4**:0.086; **4′**:0.099 **4″**:0.0758;
GOF (all data)	1.01	**3**:1.00; **3′**:0.914	**4**:1.02; **4′**:1.02 **4″**:0.845
Max. diff. peak/hole (e Å^{-3})	0.27/–0.25	**3:** 0.37/–0.55; **3′**:0.60/–0.55	**4**:0.42/–0.56 **4′**:0.47/–0.95 **4″**:0.729/–0.50

[a]**3′,** and **4′** and **4″**represent repeat structure determinations of complexes **3** and **4**, respectively, each synthesized independently; **3**, **4**, and **4′** are all made by oxygenation of Rh(H)$_2$ complexes, while **3′**, **4″** are all made by oxygenation of Rh(N$_2$) complexes.

Table S2 Selected bond lengths (Å) with estimated standard deviations in parentheses for Rh^{I} complexes: RhCl(IPr)(PPh$_3$)(O$_2$) (**2**), *trans*-RhCl(IMes)$_2$(O$_2$) (**3**),[1] *trans*-RhCl(IPr)$_2$(O$_2$) (**4**),[1] and repeat independent determinations.

Bond	**2**	**3**	**3′**^{a1}	**4**	**4′**^{a}	**4″** ^{a1}
	ccdc888671	ccdc915322	ccdc725326	ccdc915321	ccdc888672	ccdc725327
O–O	1.382(4)	1.34(4)^{b} 1.37(6)^{c}	1.24(5) 1.26(6)	1.391(6)^{b} 1.42(5)^{c}	1.379(4)^{b} 1.376(10)^{c}	1.381(9)
Rh–O1	2.027(3)	2.071(11)^{b} 2.08(2)^{c}	2.110(15) ^{b}; 2.15(2)^{c}	1.990(3)^{b} 1.95(3)^{c}	2.000(3)^{b} 2.12(3)^{c}	1.989(3) 1.995(4)
Rh–O2	1.970(3)	2.090(9)^{b} 2.091(11)^{c}	2.110(14))^{b} 2.129(15)^{c}	1.986(3)^{b} 1.92(4)^{c}	1.985(2)^{b} 2.00(2)^{c}	
Rh–Cl	2.2798(11)	2.214(5)^{b} 2.157(6)^{c}	2.217(6)^{b}, 2.205(8) ^{c}	2.2837(15)^{b} 2.276(12)^{c}	2.2960(10) ^{b}2.314(7)^{c}	2.2876(9)
Rh–C	2.032(4)^{d}	2.052(3)^{b} 2.036(3) ^{c}	2.040(3)^{b}; 2.049(3)^{c}	2.059(4) ^{b} 2.062(3) ^{c}	2.066(3) ^{b} 2.076(3) ^{c}	2.056(3)

[a] See footnote *a* of Table 1A. [b] Main fragment : [c] minor fragment within disordered Cl and O$_2$ ligands: fragment ratios are 9:1, 9:1, 3:2, and 5.6:4.4, respectively, for **4**, **4′**, **3** and **3′**.

Table S3: Selected bond angles (deg) with estimated standard deviations in parentheses for Rh^{I} complexes

Bond	**2**	**3**	**3′**^{a1}	**4**	**4′**^{a}	**4″** ^{a1}
	ccdc88671	ccdc915322	ccdc725326	ccdc915321	ccdc888672	ccdc725327
Rh–O1–O2	67.56(16)	71.9(8)^{b} 71.3(10)^{c}	73.0(11)^{b} 71.9(13)	69.36(18)^{b} 67.1(19)^{c}	69.19(14)^{b} 65.8^{c}	69.9(2)
Rh–O2–O1	72.02(16)	70.4(8)^{b} 70.3(15)^{c}	72.9(12)^{b} 73.9(17)^{c}	69.7(2)^{b} 70(2)^{c}	70.32(16)^{b} 75.2(14)^{c}	69.50(18)
O2–Rh–O1	40.42(11)	37.7(12)^{b} 38(2)^{c}	34.2(15)^{b} 34.2(19) ^{c}	41.0(2)^{b} 43.0(18)^{c}	40.49(14)^{b} 39.0(5)^{c}	40.6(3)
O1–Rh–Cl	163.22(9)	161.0(6)^{b} 163.1(9)^{c}	163.1(8)^{b} 164.7(9)^{c}	162.27(14)^{b} 159.8(11)^{c}	162.77(10)^{b} 160.3(6)^{c}	156.97(17)
O2–Rh–Cl	156.19(10)	161.3(7)^{b} 158.3(11)^{c}	162.6(8)^{b} 160.7(11) ^{c}	156.76(13)^{b} 157.1(14)^{c}	156.74(11)^{b} 160.7(6)^{c}	162.45(16)
O1–Rh–C(1)	86.56(13)	90.9(3)^{b}, 89.0(5)^{c}	90.0(4)^{b} 89.8(6) ^{c}	89.59(13)^{b} 89.1(10)^{c}	89.50(11)^{b} 89.9(7)^{c}	90.92(11)
O1–Rh–C_T^{d}	90.75(9)^{e}	89.5(3)^{b} 90.5(3)^{c}	91.1(4)^{b} 89.8(6) ^{c}	88.74(13)^{b} 91.7(9)^{c}	88.74^{b} 91.8(7)^{c}	87.51(11)
O2–Rh–C(1)	88.75(13)	91.4(3)^{b} 88.5(3)^{c}	90.5(4) ^{b} 90.3(4)^{c}	91.07(13)^{b} 89.2(11)^{c}	90.93(9)^{b} 88.9(7)^{c}	89.73(13)
O2–Rh–C_T^{d}	92.78(9)^{f}	89.5(3)^{b} 90.5(3)^{c}	90.4(4) ^{b} 88.6(4) ^{c}	87.28(13)^{b} 92.6(10)^{c}	87.53(9)^{b} 92.7(7)^{c}	88.59(13)
C–Rh–C_T	173.85(11)^{g}	179.03(14)	178.93(15)	178.23(14)	178.22(9)	178.25(11)

^{a} See footnote *a* of Table 1A. ^{b,c} See footnote *b* and *c* for Table 2A. $^{d}C_T$ represents the carbene-C trans to C(1). ^{e}O1–Rh–P angle. $^{f}O_2$–Rh–P angle. ^{g}C–Rh–P angle.

DFT Calculations

Density functional calculations were performed using ORCA version 2.8 running on multiprocessor servers (lattice) through the WestGrid supercomputing centre. Calculations for the potential energy surface were performed on simplified complexes using IMes N-heterocyclic ligands instead of the bulkier parent ligands used in our experimental work. Previous studies have shown that the nature of the RhO_2 moiety in these complexes is not largely affected by steric bulk in the NHC ligands.[1] Gas phase calculations were performed using the BP86 functional and TZVP basis set (as implemented in ORCA 2.8).[5] Constrained geometry optimizations were performed with two overall constraints: (*i*) the Rh-(O_2) distance (as referenced by a dummy atom at the midpoint between the two oxygen atoms of the ligand) and (*ii*) the O-O bond distance. Additional constraints are included to ensure that the dummy atom stays at the midpoint of the O-O bond.

An example of an input file for creation of the restricted singlet relaxed surface for $ClRh(IMe)_2O_2$ is shown below.

```
# ** Molecule: RhO2NHC2Cl singlet surface scan rOO=1.26A
# -JOB PARAMETERS-
 ! UKS BP86 TZVP RI TightSCF SlowConv SCFConv7 OPT
 ! Smallprint
 ! grid4 nofinalgrid
# -RELAXED SCAN DETAILS-
 %geom
       Scan B 5 32 = 3.00, 1.80, 25 end       # scan Rh-DA distance
       Constraints
        { B 32 33 0.63 C }                    # constrain DA-O1 distance
        { B 32 34 0.63 C }                    # constrain DA-O2 distance
        { A 33 32 34 C }                      # constrain O1-DA-O2 angle
       end
       Modify_Internal
        { A 1  5  6  R }                      # remove C-Rh-C angle (near 180degrees)
       end
       end

 # -ATOMIC COORDINATES-
  %coords  CTyp   internal
          Charge 0
          Mult   1
          coords
            N    0  0  0   0.000      0.000      0.000
            C    1  0  0   1.367      0.000      0.000
            N    2  1  0   1.367    103.980      0.000
            C    3  2  1   1.390    111.452     -0.200
            C    4  3  2   1.362    106.554      0.415
           Rh    2  3  4   2.090    128.348   -177.617
            C    6  2  3   2.086    178.892   -112.814
            N    7  6  2   1.366    126.801     64.179
            C    8  7  6   1.389    111.459   -176.876
```

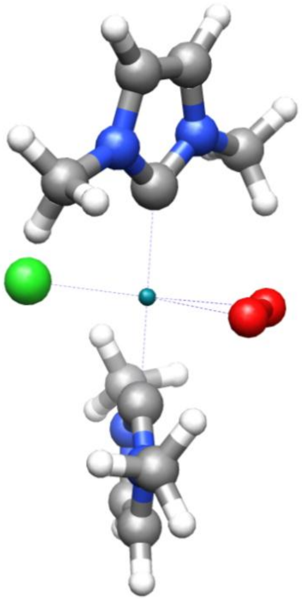
```
  C    9  8  7   1.362    106.527      0.067
  N   10  9  8   1.390    106.544     -0.268
  C    8  7  6   1.462    123.633      4.288
  C   11  7  6   1.462    124.054     -1.518
  C    3  2  6   1.462    124.164      3.865
  C    1  2  6   1.462    124.116      0.346
  H   12  8  7   1.095    109.471    -56.598
  H   12  8  7   1.095    109.471   -176.556
  H   12  8  7   1.095    109.471     63.669
  H    9  8  7   1.085    122.486    180.000
  H   10  9  8   1.085    130.991    180.000
  H   13 11  7   1.095    109.471   -150.011
  H   13 11  7   1.095    109.471    -31.087
  H   13 11  7   1.095    109.471     89.741
  H   14  3  2   1.095    109.471     91.861
  H   14  3  2   1.095    109.471    -29.205
  H   14  3  2   1.095    109.471   -147.638
  H    4  3  2   1.085    122.460    180.000
  H    5  4  3   1.085    130.974    180.000
  H   15  1  2   1.095    109.471    -33.026
  H   15  1  2   1.095    109.471   -152.026
  H   15  1  2   1.095    109.471     87.362
 Cl    6  7  8   2.366     88.932     67.820
 DA    6  7  8   1.900     90.000    250.000
  O   33  6  7   0.680     90.000     90.000
  O   33  6  7   0.680     90.000    270.000
 end
end
```

Bonding energies obtained from the above surface scans yield the following table of relative energies:

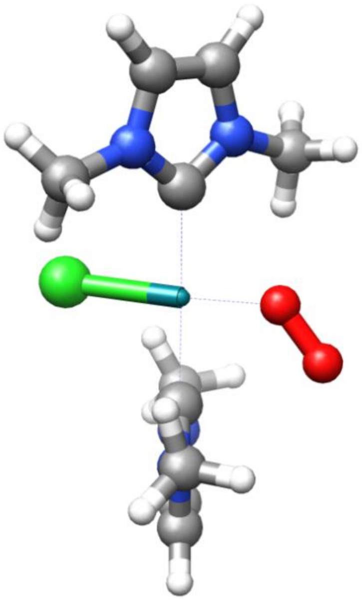
Energy (eV)	**r_{OO} (pm)**									
r_{RhO2} (pm)	126	128	130	132	134	136	138	140	142	144
80	0.621	0.506	0.413	0.341	0.285	0.246	0.221	0.208	0.207	0.215
85	0.432	0.325	0.241	0.176	0.128	0.097	0.078	0.073	0.078	0.094
90	0.324	0.224	0.147	0.089	0.048	0.022	0.010	0.011	0.022	0.043
95	0.267	0.185	0.114	0.062	0.022	**0.006**	**0.000**	**0.006**	0.022	0.048
00	0.243	0.194	0.128	0.064	0.031	0.035	0.031	0.043	0.064	0.094
05	0.251	0.237	0.176	0.092	0.076	0.098	0.077	0.114	0.138	0.172
10	0.384	0.307	0.250	0.212	0.130	0.184	0.142	0.208	0.201	0.272
15	0.346	0.301	0.279	0.263	0.268	0.288	0.297	0.318	0.349	0.326
20	0.388	0.406	0.290	0.246	0.275	0.288	0.301	0.439	0.387	0.426
25	0.332	0.306	0.297	0.303	0.322	0.357	0.393	0.431	0.476	0.530
30	0.258	0.232	0.224	0.231	0.251	0.288	0.324	0.357	0.435	0.635
35	0.214	0.188	0.179	0.186	0.207	0.244	0.280	0.336	0.392	0.741
40	0.198	0.171	**0.160**	0.169	0.189	0.225	0.262	0.318	0.374	0.528
45	0.205	0.178	0.167	0.175	0.194	0.230	0.267	0.322	0.378	0.542
50	0.231	0.203	0.194	0.200	0.219	0.256	0.292	0.341	0.400	0.583
55	0.272	0.245	0.236	0.242	0.261	0.250	0.334	0.383	0.439	0.628
60	0.325	0.299	0.290	0.296	0.316	0.347	0.389	0.439	0.495	0.562
65	0.387	0.361	0.353	0.360	0.380	0.412	0.454	0.505	0.561	0.624
70	0.455	0.430	0.422	0.430	0.452	0.484	0.527	0.578	0.635	0.699
75	0.525	0.502	0.496	0.505	0.527	0.561	0.605	0.656	0.714	0.779

80	0.597	0.575	0.570	0.580	0.604	0.639	0.684	0.735	0.795	0.861
85	0.669	0.648	0.644	0.656	0.681	0.717	0.762	0.815	0.876	0.942
90	0.738	0.719	0.717	0.730	0.756	0.793	0.839	0.894	0.956	1.024
95	0.805	0.787	0.786	0.800	0.828	0.867	0.916	0.976	1.034	1.103
00	0.868	0.852	0.853	0.868	0.897	0.938	0.995	1.050	1.109	1.179

The two minima in the potential energy surface correspond to the following structures:



A



B

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