Aerobic oxidation-induced virtual radical coupling of mixed-metal $PtRh_2$ trinuclear complexes accompanied by the formation of a Rh–Rh bond

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Supplementary Information

1. Synthesis and characterisation of the hexanuclear complex [1]Cl_2

Synthesis

All chemicals were purchased from Sigma-Aldrich, Nacalai Tesque and Wako Pure Chemical Industries. All reagents and solvents were used as received. Bis(hydrosulfido) platinum complex [Pt(bisNHC)$(SH)_2$] was prepared according to the reported procedures.[1]

A solution of the bis(hydrosulfido) platinum complex bearing a bisNHC ligand [Pt(bisNHC)$(SH)_2$] (236 mg, 0.54 mmol) in $CHCl_3$ (40 mL) was added to a solution of [Rh(nbd)Cl]$_2$ (502 mg, 1.00 mmol) in $CHCl_3$ (40 mL). After the mixture was stirred for 60 min., the solvent was removed under reduced pressure to afford a crude product as a dark green solid. The crude product was purified using a short alumina column chromatograph with a mixed solvent of CH_2Cl_2 and CH_3OH (9:1). The second fraction was collected, and the solvent of the eluate was removed under reduced pressure. The obtained solid was redissolved in CH_2Cl_2 (10 mL), and the solution was passed through the Celite. The solvent of the filtrate was removed under reduced pressure to give a chloride salt of the complex as a dark green solid. Yield 90 mg (20%).

Single crystals suitable for X-ray diffraction study was obtained by slow diffusion of toluene to a solution of the complex in a mixed solvent of CH_2Cl_2 and CH_3OH (9:1).

Elemental analysis

Elemental analysis was performed on a J-Science Lab JM-10 elemental analyser by the Analytical Research Centre at Osaka Metropolitan University. Calcd for [{Pt(bisNHC)}{Rh(nbd)}$_2$(μ_3-S)$_2$]$_2$$Cl_2$•5$H_2O$ ($C_{46}H_{66}N_8Cl_2O_5Pt_2Rh_4S_4$): C, 30.49; H, 3.61; N, 6.18, Found: C, 30.38; H, 3.61; N, 6.18.

^{1}H and ^{13}C NMR spectroscopy

^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE 600 or 400 FT-NMR spectrometers. Chemical shifts (δ in ppm, coupling constants J in Hz) for ^{1}H and ^{13}C NMR signals are expressed from $SiMe_4$ and referenced to residual solvent resonances.

^{1}H NMR (CD_3OD, 600 MHz, 293 K): δ 7.28 (d, 2H, $^3J_{H–H}$ = 2.0 Hz, 5-Im), 7.17 (d, 2H, $^3J_{H–H}$ = 2.1 Hz, 4-Im), 7.17 (d, 2H, $^3J_{H–H}$ = 2.1 Hz, 5'-Im), 7.05 (d, 2H, $^2J_{H–H}$ = 12.5 Hz, CH_2), 6.76 (d, 2H, $^3J_{H–H}$ = 2.0 Hz, 4'-Im), 5.88 (d, 2H, $^2J_{H–H}$ = 12.6 Hz, CH_2), 5.16 (br, 4H, 1',5'-nbd), 5.10 (br, 4H, 2',4'-nbd), 4.89 (br, 2H, 5-nbd), 4.29 (s, 6H, N-Me), 4.25 (br, d, 6H, J = 1.7 Hz, 1-nbd(2H), 3',6'-nbd(4H)), 3.92 (br, 2H, 6-nbd), 3.59 (s, 6H, N-Me'), 3.55 (br, 2H, 3-nbd), 2.29 (t, 2H, J = 3.7 Hz, 2-nbd), 2.03 (t, 2H, J = 3.7 Hz, 4-nbd), 1.98 (s, 4H, 7'-nbd), 1.16 (s, 4H, 7-nbd). ^{13}C NMR (CD_3OD, 150 MHz, 293 K): δ 154.8 (s, 2-Im), 152.4 (s, 2'-Im), 124.6 (s, 4'-Im), 124.2 (s, 4-Im), 122.0 (s, 5-Im), 121.0 (s, 5'-Im), 70.8 (d, $^1J_{C–Rh}$ = 7.2 Hz, 5-nbd), 70.3 (d, $^1J_{C–Rh}$ = 5.6 Hz, 1-nbd), 70.1 (d, $^2J_{C–Rh}$ = 3.7 Hz, 2-nbd), 65.2 (d, $^1J_{C–Rh}$ = 6.2 Hz, 7'-nbd), 63.3 (s, CH_2), 62.9 (s, 7-nbd), 62.5 (br, 2',4'-nbd), 61.0 (br, 1',5'-nbd), 58.6 (d, $^1J_{C–Rh}$ = 6.2 Hz, 4-nbd), 52.7 (s, 3',6'-nbd), 50.0 (s, 6-nbd), 49.5 (s, 3-nbd), 39.5 (s, N-Me), 37.7 (s, N-Me').

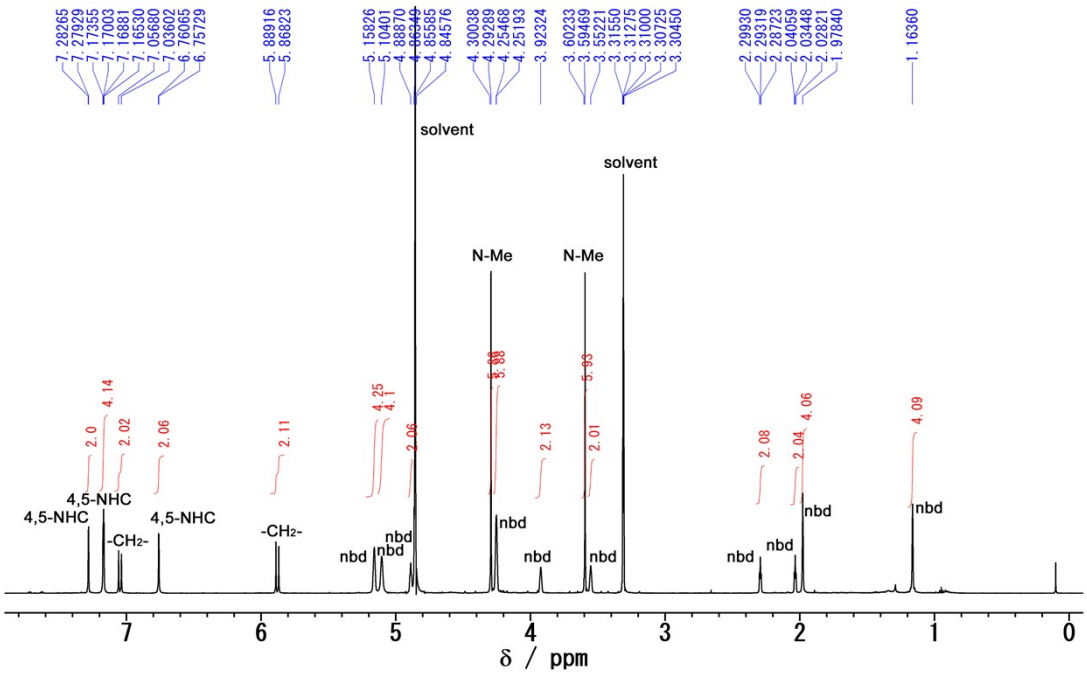

Fig. S1 ^{1}H NMR spectrum of hexanuclear complex [**1**]Cl_2 (CD_3OD, 600 MHz, 293 K).

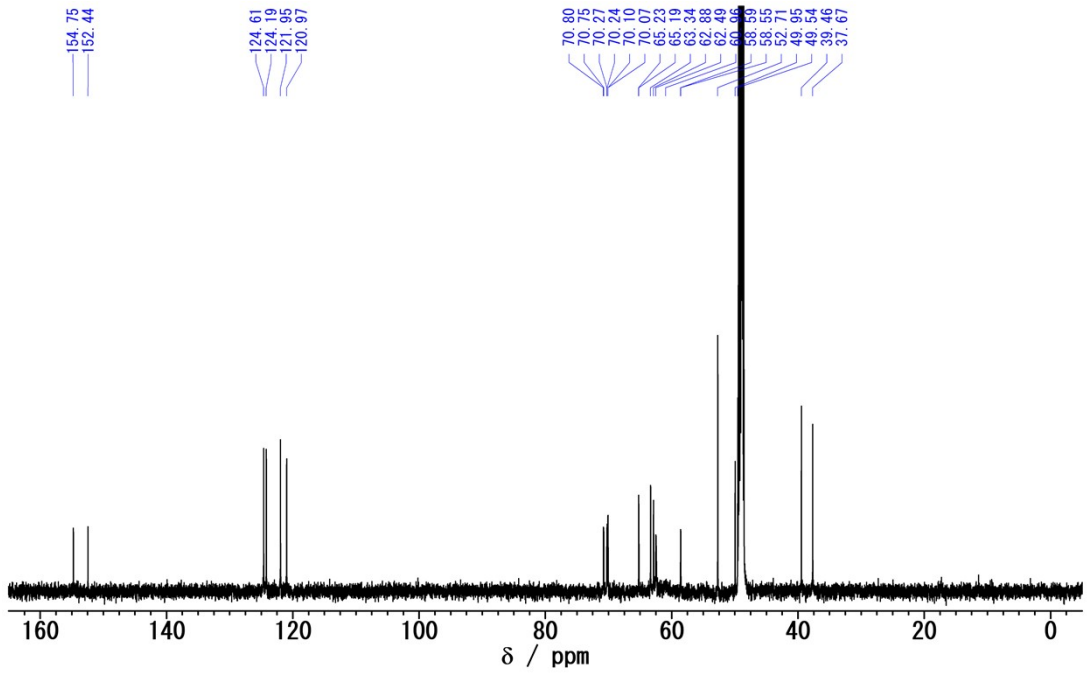

Fig. S2 ^{13}C NMR spectrum of hexanuclear complex [**1**]Cl_2 (CD_3OD, 150 MHz, 293 K).

Electrospray ionisation mass spectrometry

Electrospray ionisation mass spectrometry was performed on JEOL AccuTOF LC-plus JMS-T100LP spectrometer using a HPLC grade CH_3OH solvent.

MS (ESI+, CH_3OH): *m/z* = 824.91 (824.95 calcd. for $[[\mathbf{1}]/2]^+$), 778.88 (778.92 calcd. for $[[\mathbf{1}] - nbd]^{2+}$), 1686.76 (1686.49 calcd. for $[[\mathbf{1}] + Cl]^+$).

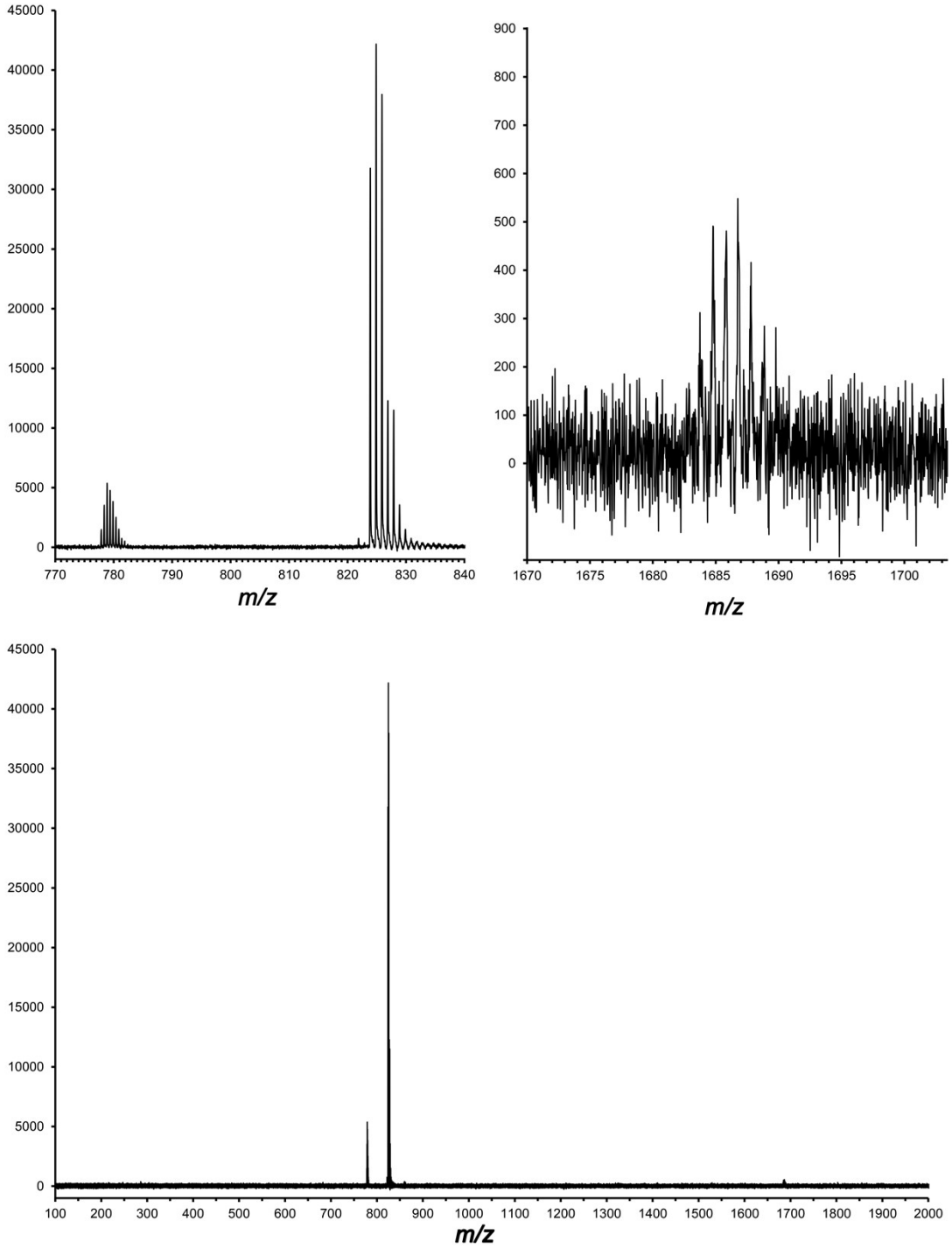

Fig. S3 ESI-mass spectrum of hexanuclear complex $[\mathbf{1}]Cl_2$ in CH_3OH.

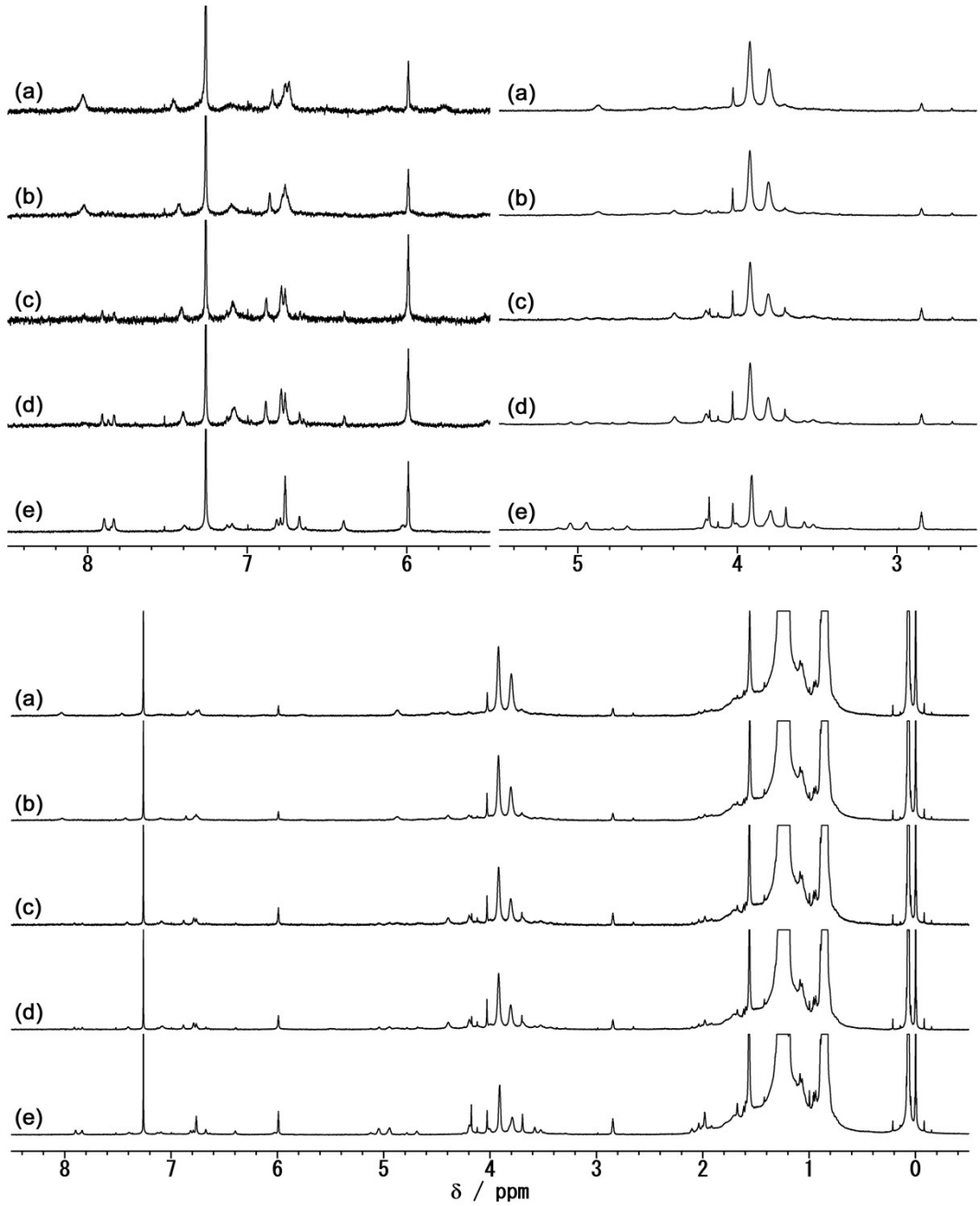

Fig. S4 ^{1}H NMR spectra of a reaction mixture of the Pt bis(hydrosulfido) and Rh nbd complexes in $CDCl_3$ under an inert atmosphere (400 MHz). (a) 10 min. and (b) 20 min. after the reaction started. (c) 35 min. after the reaction started and 5 min. after the mixture was exposed to air. (d) 15 min. and (e) 500 min. after the mixture was exposed to air.

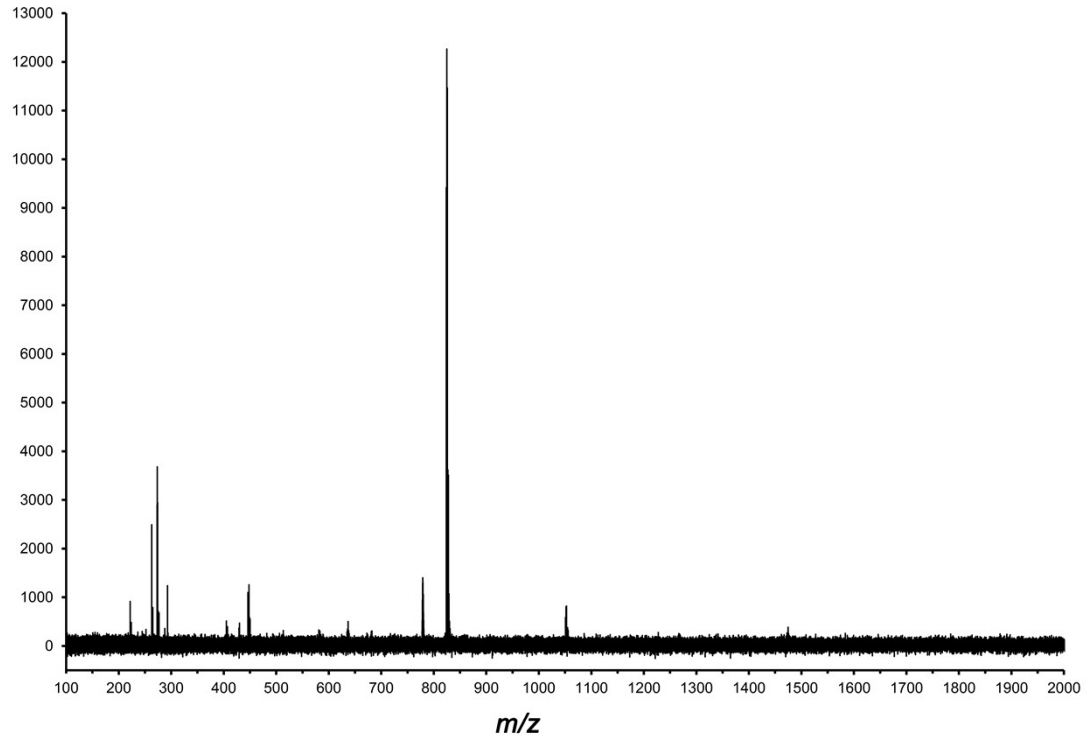

Fig. S5 ESI-mass spectrum of the green reaction mixture obtained after exposing to air (diluted with CH_3OH).

2. Cyclic voltammetry

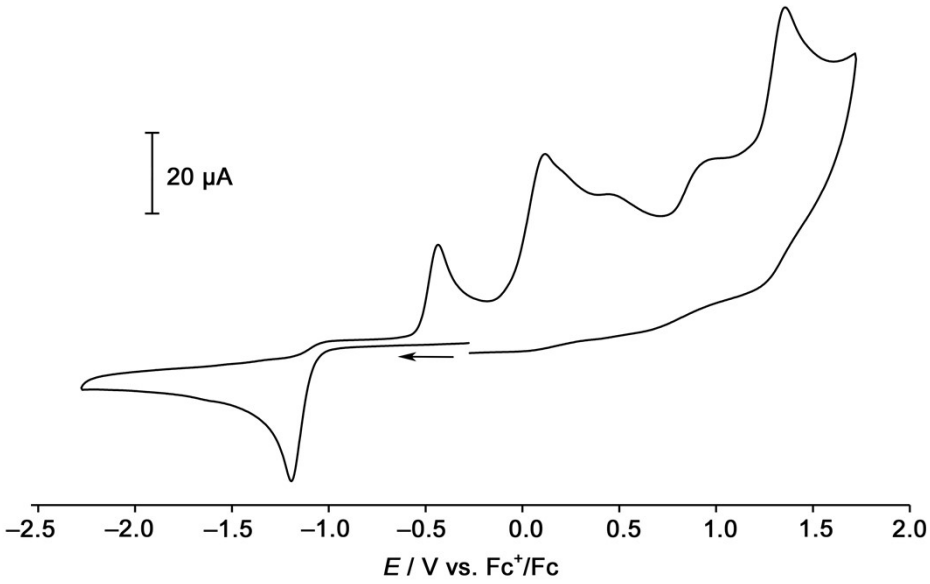

Fig. S6 Cyclic voltammogram of [**1**]Cl_2 (1.0 mmol L^{-1}) in CH_3CN containing 0.10 mol L^{-1} of *n*-BuN_4PF_6 as a supporting electrolyte with a 100 mV s^{-1} scan rate.

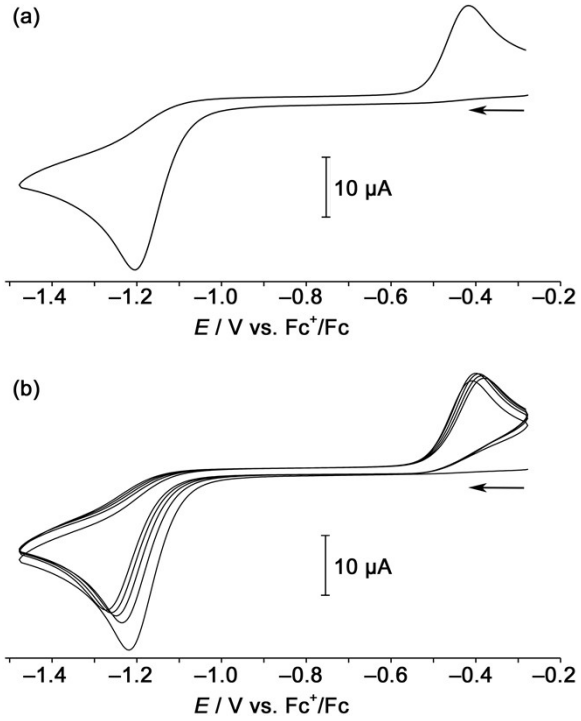

Fig. S7 Cyclic voltammograms of [**1**]Cl_2 (1.0 mmol L^{-1}) with (a) normal and (b) repeated scans in CH_3CN containing 0.10 mol L^{-1} of *n*-BuN_4PF_6 as a supporting electrolyte with a 100 mV s^{-1} scan rate.

3. The reduction of the hexanuclear complex using decamethylcobaltocene and reoxidation upon exposure to air monitored using ^{1}H NMR spectroscopy.

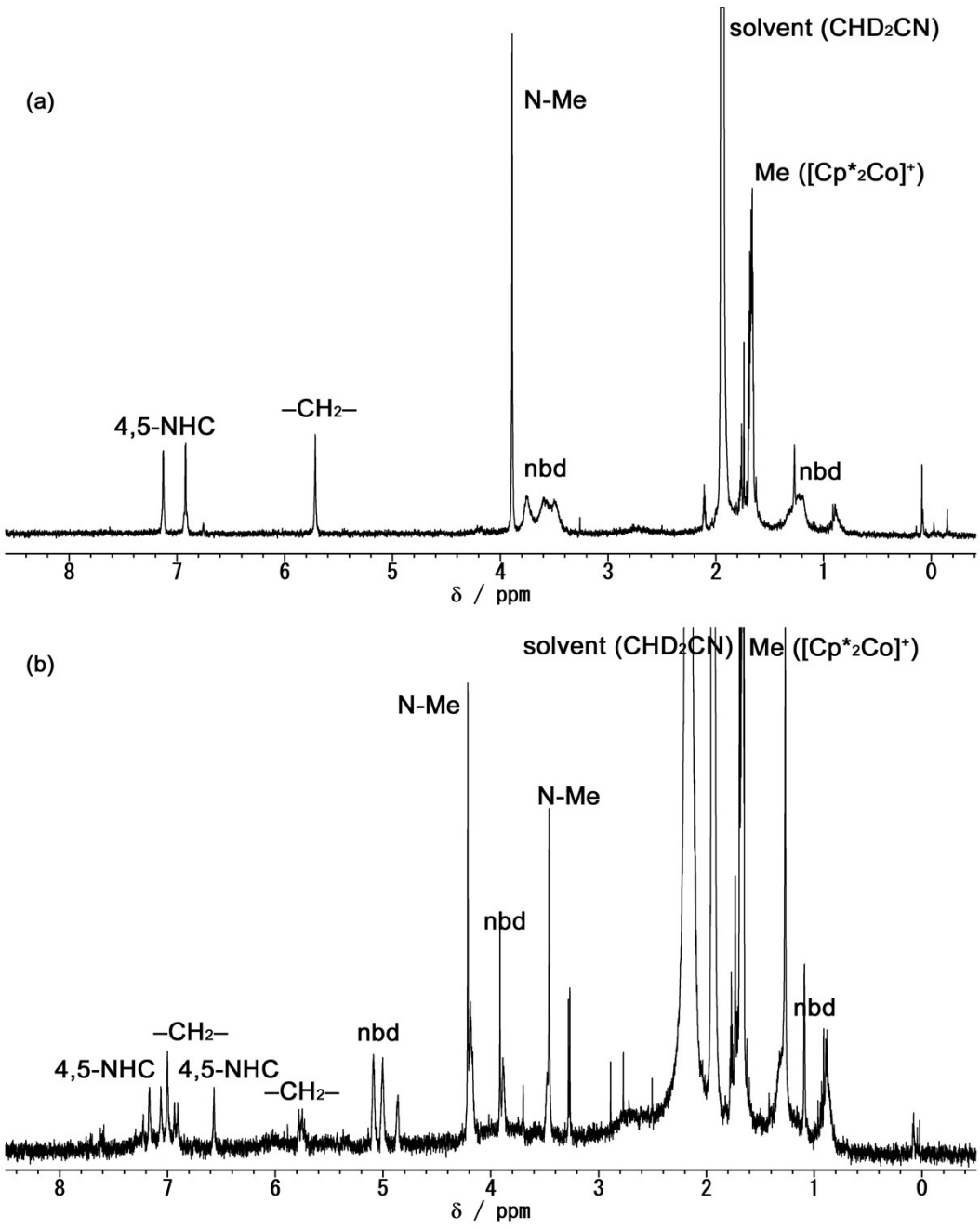

Fig. S8 ^{1}H NMR spectra of a reaction mixture of [**1**]Cl_2 (a) with decamethylcobaltocene under an inert atmosphere and (b) after exposure to air (CD_3CN, 400 MHz, 293 K).

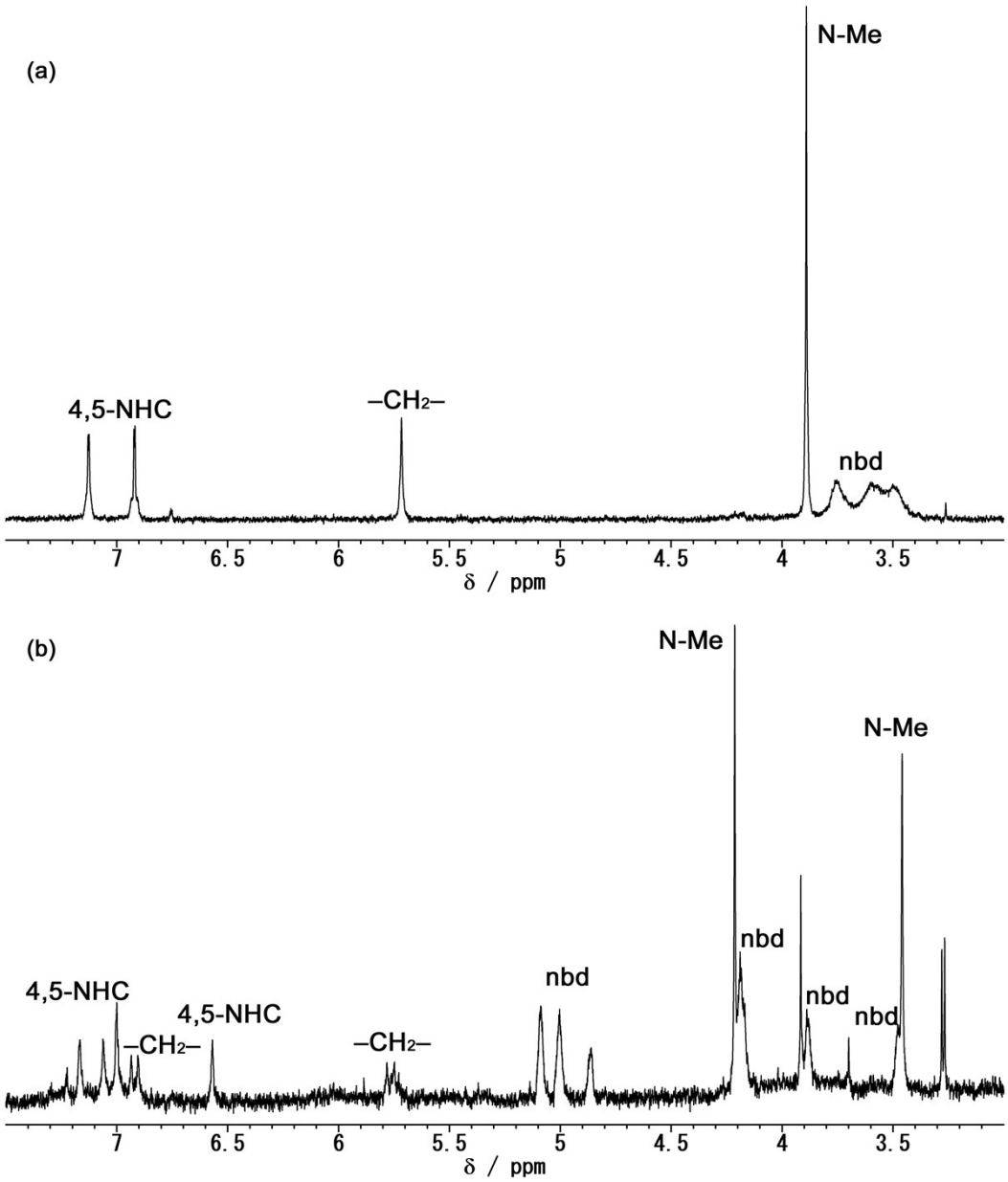

Fig. S9 Expanded ^{1}H NMR spectra of a reaction mixture of [**1**]Cl_2 (a) with decamethylcobaltocene under inert atmosphere and (b) after exposure to air (CD_3CN, 400 MHz, 293 K).

4. X-ray crystallography

A single crystal of the complex was mounted on a loop using Paratone. Diffraction data were collected on a Rigaku Varimax Saturn724+ diffractometer using a rotation method with 0.5° frame widths. The data were integrated, scaled, sorted, and averaged. Absorption corrections were applied using the multi-scan method. The structures were solved using SIR97[2] and refined with SHELXL Version 2018/3[3]. [1] All hydrogen atoms were located at the calculated positions and refined as riding models. Crystallographic data are summarised in Tables S1 for hexanuclear complex [**1**]Cl_2. The structure of the complex contains positionally disordered Cl anions and solvent molecules. Because of the difficulty for the sufficient refinement, the solvent mask was applied using PLATON/SQUEEZE.[4]

Table S1. Crystallographic data of hexanuclear complex [**1**]Cl_2•toluene[+ solvent] (CCDC 2411823).

Formula	$C_{53}H_{64}Cl_2N_8Pt_2Rh_4S_4$ [+ solvent]
M_w	1814.08
Crystal description	dark green, prism
Crystal size/mm	0.190 × 0.030 × 0.010
Crystal system	*triclinic*
Space group	$P\bar{1}$ (#2)
a/Å	11.5306(2)
b/Å	15.1580(3)
c/Å	18.8117(4)
α/°	99.366(2)
β/°	95.802(2)
γ/°	108.839(2)
V/Å^3	3028.46(11)
Z	2
F(000)	1744.00
ρ_{calcd}/g cm^{-1}	1.989
μ/mm^{-1}	5.934
Total reflections	31574
Unique reflections (R_{int})	13774 (0.0339)
Scan range θ/°	2.003 to 27.500
Completeness	0.996
Index ranges	–14≤ h ≤ 14
	–19 ≤ k ≤ 19
	–24 ≤ l ≤ 24
Data/restrains/para.	13774/85/726
*R*1 [*I*>2σ(*I*)], *wR*2 (all data)	0.0352, 0.0867
GOF on F^2	1.034
Max./min. ρ/eÅ^{-3}	2.772/–0.873
Min./max. *T*	0.5799/1.0000

5. DFT calculations

DFT calculations were carried out on the hexanuclear [**1**]$^{2+}$, monocationic [**2**]$^{\bullet+}$ and neutral [**2**] complexes using Gaussian16.[5] Atomic coordinates were optimised at the level of B3LYP ([**1**]$^{2+}$ and [**2**]) or UB3LYP ([**2**]$^{\bullet+}$) with LanL2DZ for Pt and Rh and 6-31G(d,p) for the others. Structural optimisations were started from the structures obtained from crystallographic analysis for [**1**]$^{2+}$ and the half of the hexanuclear complex for [**2**]$^{\bullet+}$ and [**2**]. Vibrational frequencies were calculated for all converged structures, and no imaginary frequencies appeared showing that these structures lie on minima. The atomic coordinates of the optimised structures of the complexes are listed in Tables S2–4.

Table S2. Optimised atomic coordinates of hexanuclear complex [**1**]$^{2+}$ obtained from DFT calculations.

Number	atom	x	y	z
1	Pt	–1.761932	–1.025889	–1.093655
2	Pt	1.761780	–1.027484	1.092328
3	Rh	0.952996	1.555086	–1.386215
4	Rh	3.577483	0.658383	–0.600594
5	Rh	–3.577315	0.657567	0.601654
6	Rh	–0.952851	1.553536	1.388057
7	S	–1.760764	1.412165	–0.894414
8	S	1.760560	1.410860	0.896205
9	S	–1.771498	–0.725703	1.336653
10	S	1.771875	–0.724167	–1.337565
11	N	2.453654	–4.016626	0.463427
12	C	–1.780562	–3.057052	–1.155461
13	N	–2.577645	–0.503670	–4.079520
14	C	–2.328705	–1.042468	–5.338114
15	C	5.409876	1.400342	0.389818
16	C	–5.410002	1.400216	–0.387748
17	N	1.086706	–3.750436	2.102903
18	C	1.635565	3.661186	–1.828894
19	C	–5.014639	2.344220	0.561696
20	C	–3.443764	–3.788165	0.583802
21	C	3.444059	–3.787555	–0.588717
22	C	–0.309118	–3.061572	–3.131783
23	C	1.329631	–5.114968	2.018673
24	C	0.308922	–3.066079	3.127549
25	C	–2.077930	3.378768	3.286391
26	C	5.742057	1.975579	–1.869497
27	C	–0.250085	3.692903	1.843419
28	C	–5.019258	0.660552	2.244105
29	C	–0.183072	3.422394	–3.293351
30	C	–5.741990	1.973080	1.872189
31	C	0.964564	4.132235	–4.063202
32	N	–1.086723	–3.747383	–2.107998
33	C	–2.185405	–5.278447	–0.987935
34	C	–0.224257	1.940019	3.481571
35	C	0.250117	3.695025	–1.839001
36	C	5.014471	2.345246	–0.558710
37	N	–1.156635	–2.095277	–3.815072
38	C	1.780633	–3.058760	1.151392
39	C	–0.964470	4.127458	4.068161
40	C	–1.635534	3.659051	1.833320
41	C	0.183165	3.418561	3.297438
42	N	2.577028	–0.509204	4.078962

43	C	1.855778	–1.152033	3.124184
44	C	–1.856230	–1.147682	–3.125674
45	N	1.156262	–2.100648	3.812231
46	C	2.078025	3.382660	–3.282284
47	C	–1.436209	–2.049211	–5.174271
48	N	–2.453321	–4.015899	–0.468602
49	C	–5.415784	–0.291324	1.289622
50	C	2.328086	–1.049764	5.336799
51	C	–1.329444	–5.112061	–2.025491
52	C	–1.616801	1.917648	3.472982
53	C	5.019601	0.663317	–2.242854
54	C	–3.585333	0.533016	–3.849320
55	C	1.435718	–2.056385	5.171529
56	C	7.082255	1.421928	–1.311528
57	C	3.584760	0.527745	3.850164
58	C	5.416167	–0.289474	–1.289290
59	C	–7.082162	1.419766	1.313828
60	C	1.616957	1.921743	–3.470628
61	C	0.224399	1.944083	–3.479206
62	C	6.382706	0.441510	–0.330688
63	C	2.185784	–5.279890	0.981043
64	C	–6.382568	0.440479	0.331891
65	H	2.805855	–0.671383	6.226741
66	H	0.972827	–2.717994	5.886679
67	H	3.368630	1.028411	2.909214
68	H	4.581130	0.078570	3.816842
69	H	3.542509	1.250215	4.667489
70	H	–0.051627	–3.798510	3.849803
71	H	–0.531340	–2.541157	2.663296
72	H	3.317681	–2.779539	–0.976905
73	H	3.292567	–4.513255	–1.390865
74	H	4.452164	–3.907943	–0.182474
75	H	0.874562	–5.832512	2.683209
76	H	2.632926	–6.172360	0.572230
77	H	–3.316674	–2.781015	0.974009
78	H	–3.292999	–4.515625	1.384485
79	H	–4.451894	–3.906926	0.177137
80	H	0.051413	–3.792971	–3.855092
81	H	0.531158	–2.537198	–2.666931
82	H	–3.543510	1.256186	–4.666046
83	H	–3.368770	1.032908	–2.908056
84	H	–4.581667	0.083764	–3.815913
85	H	–2.806661	–0.663006	–6.227494
86	H	–0.973289	–2.709779	–5.890366
87	H	–2.632348	–6.171514	–0.580213
88	H	–0.874361	–5.828685	–2.691010
89	H	5.303329	1.477888	1.464281
90	H	4.539162	3.2980	–0.362231
91	H	5.783932	2.746106	–2.638758
92	H	7.682368	2.184068	–0.803233
93	H	7.685759	0.912878	–2.070487
94	H	7.006226	–0.187037	0.304447
95	H	5.350322	–1.365848	–1.388506
96	H	4.580879	0.458954	–3.211937
97	H	0.407106	4.053547	1.066020
98	H	1.211191	3.674248	3.547058
99	H	–0.968069	3.902488	5.139903
100	H	–0.984386	5.211048	3.911912

101	H	–3.118523	3.592755	3.525042
102	H	0.436340	1.150554	3.809163
103	H	–2.257773	1.107282	3.792835
104	H	–2.293671	3.987484	1.039924
105	H	–7.682472	2.182324	0.806392
106	H	–7.685481	0.909831	2.072339
107	H	–5.783894	2.742801	2.642254
108	H	–4.539522	3.297259	0.366137
109	H	–5.303562	1.478880	–1.462136
110	H	–7.006060	–0.187521	–0.303811
111	H	–5.349737	–1.367789	1.387704
112	H	–4.580370	0.455267	3.212917
113	H	2.257958	1.111822	–3.791556
114	H	3.118618	3.596982	–3.520634
115	H	–0.436132	1.155018	–3.807897
116	H	0.984435	5.215645	–3.905694
117	H	0.968199	3.908514	–5.135205
118	H	–1.211096	3.678353	–3.542703
119	H	–0.407107	4.054691	–1.061179
120	H	2.293664	3.988599	–1.035047

Table S3. Optimised atomic coordinates of trinuclear complex [**2**]$^{\bullet+}$ obtained from DFT calculations.

Number	atom	x	y	z
1	Rh	–1.624894	–1.357071	0.000042
2	Pt	1.412664	–0.151297	0.000011
3	S	–0.444635	–0.007598	1.567238
4	S	–0.444630	–0.007692	–1.567231
5	N	4.038186	0.564581	1.194839
6	N	3.070518	–0.773361	2.574172
7	N	4.038167	0.564405	–1.194958
8	N	3.070459	–0.773703	–2.574101
9	C	–2.474595	–3.016713	1.206979
10	C	–2.474591	–3.016785	–1.206799
11	C	2.889418	–0.150447	–1.383864
12	C	4.920266	0.396451	–2.254911
13	H	5.88250	0.881547	–2.299049
14	C	4.304204	–0.442403	–3.123421
15	H	4.631936	–0.835687	–4.072615
16	C	2.124591	–1.687003	–3.217102
17	H	1.425557	–2.050646	–2.467394
18	H	2.678249	–2.524784	–3.646080
19	H	1.569157	–1.167891	–4.001034
20	C	4.253164	1.366878	–0.000122
21	C	2.889433	–0.150232	1.383873
22	C	4.920342	0.396704	2.254755
23	H	5.882616	0.881733	2.298764
24	C	4.304175	–0.441798	3.123531
25	H	4.631864	–0.834836	4.072841
26	C	2.12470	–1.686635	3.217284
27	H	1.425777	–2.050533	2.467596
28	H	1.569134	–1.167408	4.001047
29	H	2.678418	–2.524252	3.646506
30	C	–2.830042	–3.919448	0.000117
31	C	–3.401527	–1.977678	1.200140
32	C	–3.401523	–1.977749	–1.200023
33	C	–4.339612	–2.232544	0.000065
34	H	–1.818403	–3.297193	2.021584

35	H	–3.597379	–1.275755	–2.000476
36	Rh	–1.310577	1.559484	–0.000044
37	C	–2.904153	2.565135	1.200208
38	C	–1.765099	3.365664	1.207694
39	C	–1.905243	4.325117	–0.000128
40	C	–1.765095	3.365591	–1.207893
41	C	–2.904149	2.565063	–1.200363
42	C	–3.759421	3.026706	–0.000092
43	H	–3.254081	1.925154	2.000110
44	H	–1.058933	3.484547	–2.020426
45	H	–1.818398	–3.297313	–2.021385
46	H	–3.597384	–1.275636	2.000550
47	C	–4.378910	–3.786613	0.000110
48	H	–5.284209	–1.689782	0.000047
49	H	–2.395615	–4.918588	0.000147
50	H	–3.254074	1.925034	–2.000227
51	H	–1.254687	5.199059	–0.000154
52	H	–1.058939	3.484669	2.020223
53	C	–3.443637	4.548679	–0.000138
54	H	–4.803014	2.713899	–0.000085
55	H	–3.803130	5.061998	–0.898316
56	H	–3.803133	5.062052	0.898009
57	H	–4.846037	–4.204501	0.898242
58	H	–4.846034	–4.204554	–0.897998
59	H	5.278560	1.737004	–0.000162
60	H	3.558783	2.210774	–0.000182

Table S4. Optimised atomic coordinates of trinuclear complex [**2**] obtained from DFT calculations.

Number	atom	x	y	z
1	Rh	1.694534	–1.385369	0.000016
2	Pt	–1.290772	–0.163231	0.000067
3	S	0.534520	0.032798	–1.569542
4	S	0.534467	0.032622	1.569761
5	N	–3.948887	0.415815	–1.194281
6	N	–2.914533	–0.862203	–2.582197
7	N	–3.949166	0.415474	1.193960
8	N	–2.915185	–0.862903	2.581825
9	C	2.302008	–3.101946	–1.191579
10	C	2.301811	–3.102401	1.191024
11	C	–2.755562	–0.231316	1.386882
12	C	–4.830847	0.192427	2.244559
13	H	–5.820136	0.620497	2.280476
14	C	–4.172195	–0.606556	3.119093
15	H	–4.482555	–1.015313	4.067622
16	C	–1.923844	–1.722188	3.225039
17	H	–1.163897	–1.981114	2.490194
18	H	–2.420227	–2.623285	3.595688
19	H	–1.441987	–1.194825	4.051414
20	C	–4.182439	1.209375	–0.000078
21	C	–2.755273	–0.230982	–1.387029
22	C	–4.830191	0.193255	–2.245301
23	H	–5.819504	0.621257	–2.281331
24	C	–4.171279	–0.605473	–3.119884
25	H	–4.481339	–1.013909	–4.068648
26	C	–1.922650	–1.720791	–3.225534
27	H	–1.166105	–1.984861	–2.489001
28	H	–1.436295	–1.190875	–4.047608

29	H	–2.419798	–2.619002	–3.602068
30	C	2.585816	–4.046392	–0.000417
31	C	3.336980	–2.151718	–1.191235
32	C	3.336788	–2.152165	1.191176
33	C	4.253602	–2.515203	–0.000035
34	H	1.634449	–3.333158	–2.012756
35	H	3.620524	–1.498755	2.006934
36	Rh	1.290560	1.699839	0.000175
37	C	2.649779	2.900188	–1.191010
38	C	1.385776	3.513771	–1.191087
39	C	1.387418	4.500092	0.000253
40	C	1.385615	3.513689	1.191554
41	C	2.649683	2.900238	1.191615
42	C	3.423890	3.511029	0.000352
43	H	3.108704	2.355295	–2.006804
44	H	0.674734	3.535480	2.008536
45	H	1.634099	–3.333933	2.011989
46	H	3.620744	–1.497860	–2.006625
47	C	4.138654	–4.063955	–0.000310
48	H	5.250807	–2.072798	0.000123
49	H	2.061674	–5.003663	–0.000654
50	H	3.108438	2.355214	2.007414
51	H	0.610890	5.267043	0.000231
52	H	0.675035	3.535588	–2.008189
53	C	2.869931	4.961763	0.000332
54	H	4.506201	3.373678	0.000394
55	H	3.144334	5.526524	0.899755
56	H	3.144420	5.526527	–0.899062
57	H	4.563569	–4.526213	–0.899727
58	H	4.563459	–4.526533	0.898992
59	H	–5.214959	1.561731	–0.000137
60	H	–3.494554	2.059728	0.000128

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