Supporting Information

First Metal Complexes of 6,6'-Dihydroxy-2,2'-bipyridine: From Molecular Wires to Applications in Carbonylation Catalysis

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Experimental details

Solvents and Reagents

Diethyl ether and tetrahydrofuran were dried by prolonged reflux, under a nitrogen atmosphere, over sodium metal with a benzophenone ketyl indicator and distilled freshly prior to use. Dichloromethane and acetonitrile were treated in a similar manner, but using calcium hydride as the drying agent. Toluene and pentane were dried by passing through a column, packed with commercially available Q-5 reagent (13 % CuO on alumina) and activated alumina (pellets, 3 mm), in a stream of nitrogen. Methyl acetate was dried over P_2O_5 and distilled under nitrogen. Acetone was dried over B_2O_3 and distilled under nitrogen. The starting materials $[Rh(CO)_2Cl]_2$,[1] $[Rh(cod)Cl]_2$,[2] and 2,2'-dipyridone,[3] were prepared according to published procedures.

References:

1) J.A. McCleverty, G. Wilkinson, *Inorg. Synth.* 1966, **8**, 211.
2) G. Giordano, R.H. Crabtree, *Inorg. Synth.* 1990, **28**, 88.
3) T. Umemoto, M. Nagayoshi, K. Adachi, G, Tomizawa, *J. Org. Chem.* 1998, **63**, 3379.

6,6'-di(t-butyldimethylsiloxy)-2,2'-bipyridine: A 50 ml, two-neck round bottom flask was loaded with 2,2'-bipyridone (0.78 g, 4.14 mmol). After the addition of t-butyldimethylsilylchloride (2.5 g, 16.6mmol), a stirrer bar and a reflux condenser, a nitrogen atmosphere was introduced. Dry triethylamine was added with stirring during which time a grey emulsion formed. The mixture was subsequently refluxed overnight. The resulting suspension was filtered under reduced pressure and the remaining solid washed with a further 10 ml of triethylamine after which the solvent was removed under reduced pressure. The resulting beige solid was dissolved in hot methanol, allowed to cool to RT and then cooled to -20 °C to induce crystallisation. The white solid was rapidly filtered and washed with two portions of cold methanol and dried under vacuum and stored in a glove box. Yield: 0.54 g (31%). Anal. Calcd. For $C_{22}H_{36}N_2O_2Si_2$: C, 63.41; H, 8.71; N, 6.72. Found: C, 63.50; H, 8.82; N, 6.79. ^1H NMR (CD_2Cl_2): 0.42 (s, 12H, $Si(CH_3)_2$), 1.03 (s, 18H, $SiC(CH_3)_3$), 6.71 (dd, 2H, J = 0.8, 8.1 Hz, Ar–*H*), 7.69 (t, 2H, J = 7.8 Hz Ar–*H*), 7.92 (dd, 2H, J = 0.8, 7.5 Hz, Ar–*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): -4.5, 17.9, 25.6, 112.9, 113.6, 139.8, 153.7, 162.2. MS (CI, *m/z* (%)): 417 (100) $[(M+H)^+]$.

[Rh(COD)(6,6'-dihydroxy-2,2'-bipyridine)]SbF$_6$: [Rh(**1**)(cod)]SbF$_6$

AgSbF$_6$ (0.131 g, 0.38 mmol) was dissolved in acetone (10 ml) and added to [Rh(COD)Cl]$_2$ (0.094 g, 0.19 mmol) to form a light yellow solution and a white precipitate. The suspension was stirred for 20 minutes before filtering. The filtrate was added to 6,6'-bis({*tert*-butyldimethylsilyloxy)-2,2'-bipyridine (0.158 g, 0.38 mmol) dissolved in de-oxygenated technical grade acetone (30 ml). The resultant dark orange solution was stirred for 30 minutes before concentrating (ca. 2 ml) and adding pentane (30 ml) to afford the product as a yellow precipitate (0.246 g, 75 %). The solid was isolated by filtration, washed with pentane (2x3 ml portions) and dried *in vacuo*.

Anal. for $C_{18}H_{20}N_2O_2F_6SbRh$ Found: C, 33.97; H, 3.20; N 4.35 %. Calculated: C, 34.05; H, 3.17; N, 4.41 %. ^{1}H-NMR (400 MHz, $(CD_3)_2CO$, J values in Hz): δ 11.58 (br, O*H*); 8.02 (t, 2H, ^3J = 7.9, Ar-*H*); 7.92 (d, 2H, ^3J = 7.9, Ar-*H*); 7.05 (d, 2H, ^3J = 7.9, Ar-*H*); 5.34 (br, 4H, C*H*); 2.39 (m, 4H, C*H*$_2$); 1.89 (q, 4H, ^3J = 8.2, C*H*$_2$). ^{13}C{^{1}H}-NMR (101 MHz, $(CD_3)_2CO$, J values in Hz): δ 168.5 (Ar C_{ipso}), 156.8 (Ar C_{ipso}), 144.8, 117.3, 115.3, 85.0 (d, $^1J_{C\text{-}Rh}$ = 12.5, Rh-*C*H), 32.2 (*C*H$_2$). ^{19}F-NMR (377 MHz, $(CD_3)_2CO$): δ -123 (superposition of sextet due to $^{121}SbF_6^-$ and octet due to $^{123}SbF_6^-$). IR (nujol): ν(OH) 3375 cm^{-1}. FAB/MS$^+$ (m/z): 399 ([M]$^+$, 100 %). FAB/MS$^-$ (m/z): 235 ([M]$^-$, 100 %).

[Rh(CO)$_2$(6,6'-dihydroxy-2,2'-bipyridine)]SbF$_6$: [Rh(**1**)(CO)$_2$]SbF$_6$

AgSbF$_6$ (0.118 g, 0.344 mmol) was dissolved in acetone (10 ml) and added to [Rh(COD)Cl]$_2$ (0.085 g, 0.172 mmol) to form a light yellow solution and a white precipitate. The suspension was stirred for 20 minutes before filtering. The filtrate was added to 6,6'-bis({*tert*-butyldimethylsilyloxy)-2,2'-bipyridine (0.144 g, 0.344 mmol) dissolved in de-oxygenated technical grade acetone (30 ml). The resultant dark orange solution was stirred for 30 minutes before concentrating (ca. 2 ml) and adding pentane (30 ml) to afford a yellow precipitate which was isolated by filtration. The yellow precipitate was dissolved in dichloromethane (15 ml) and CO was bubbled through the solution for 30 minutes whilst stirring. The solution turns green, while a purple solid starts precipitating. The dichloromethane solution was reduced to 2 ml before adding pentane (30 ml) to afford the product as a purple solid (0.162 g, 81 %). The solid was isolated by filtration, washed with pentane (2x5 ml portions) and dried *in vacuo*.

Anal. for $C_{12}H_8N_2O_4F_6SbRh$ Found: C, 24.82; H, 1.43; N 4.74 %. Calculated: C, 24.73; H, 1.38; N, 4.81 %. ^{1}H-NMR (400 MHz, $(CD_3)_2CO$, J values in Hz): δ 12.87 (br, OH); 8.17 (t, 2H, ^3J = 8.0, Ar-H); 7.96 (d, 2H, ^3J = 8.0, Ar-H); 7.30 (d, 2H, ^3J = 8.0, Ar-H). ^{13}C{^{1}H}-NMR (101 MHz, $(CD_3)_2CO$, J values in Hz): δ 114.3, 116.8, 145.7, 155.6 (Ar C_{ipso}), 164.3 (Ar C_{ipso}), 184.3 (d, $^1J_{\mathrm{C\text{-}Rh}}$ = 70.9, Rh-CO). ^{19}F-NMR (377 MHz, $(CD_3)_2CO$): δ -123 (superposition of sextet due to $^{121}SbF_6^-$ and octet due to $^{123}SbF_6^-$). IR (nujol) (OH) 3324 cm^{-1}, ν(CO), 2108, 2052 cm^{-1}. FAB/MS$^+$ (m/z): 347 ([M]$^+$, 100 %). FAB/MS$^-$ (m/z): 235 ([M]$^-$, 100 %).

[Rh(CO)$_2$(2-(2'-(6'-hydroxypyridyl)-6-pyridone))]: [Rh(**1'**)(CO)$_2$]

[Rh(CO)$_2$(6,6'-dihydroxy-2,2'-bipyridine)]SbF$_6$ (50 mg, 0.085 mmol) was suspended in methanol (150ml) before adding KOH (4.8 mg, 0.085 mmol) dissolved in ethanol (1ml). The resultant suspension was stirred for an hour before isolating the product by filtration. The resultant purple solid was dried under vacuum (68 % yield).

Anal. for $C_{12}H_7N_2O_4Rh$ Found: C, 41.44; H, 2.05; N 7.90 %. Calculated: C, 41.64; H, 2.04; N, 8.09 %. IR (nujol) (OH) 3422 cm^{-1}, ν(CO), 2072, 2002 cm^{-1} ν(C=O), 1610 cm^{-1}.

K[Rh(CO)$_2$(2,2'-bipyridone)]: K[Rh(**1''**)(CO)$_2$]

[Rh(CO)$_2$(2-(2'-(6'-hydroxypyridyl)-6-pyridone))] (25 mg, 0.072 mmol) was suspended in ethanol (50ml) before adding KOH (4.1 mg, 0.072 mmol) dissolved in ethanol (1ml). The resultant yellow solution was stirred for 3 hours before the ethanol was removed under vacuum to give the product as a red solid in 89 % yield.

Anal. for $C_{12}H_6N_2O_4KRh$ Found: C, 37.35; H, 1.45; N 7.15 %. Calculated: C, 37.52; H, 1.57; N, 7.29 %. ^{1}H-NMR (400 MHz, d$_6$-dmso, J values in Hz): 7.16 (dd, 2H, ^3J = 6.8, 8.7 Ar-H); 6.51 (d, 2H, ^3J = 6.8, Ar-H); 6.11 (d, 2H, ^3J = 8.7, Ar-H). ^{13}C{^{1}H}-NMR (101 MHz, d$_6$-dmso, J values in Hz): δ 101.8, 116.03, 138.19, 157.42 (Ar C_{ipso}), 166.73 (Ar C_{ipso}), 188.45 (d, $^1J_{\mathrm{C\text{-}Rh}}$ = 68.1, Rh-CO). IR (nujol) ν(CO), 2047, 1966 cm^{-1}, ν(C=O), 1620 cm^{-1}. ESI/MS$^-$ (m/z): 345 ([M]$^-$, 100 %).

NMR Spectroscopy

Selected spectra for all complexes are provided in the following Figures.

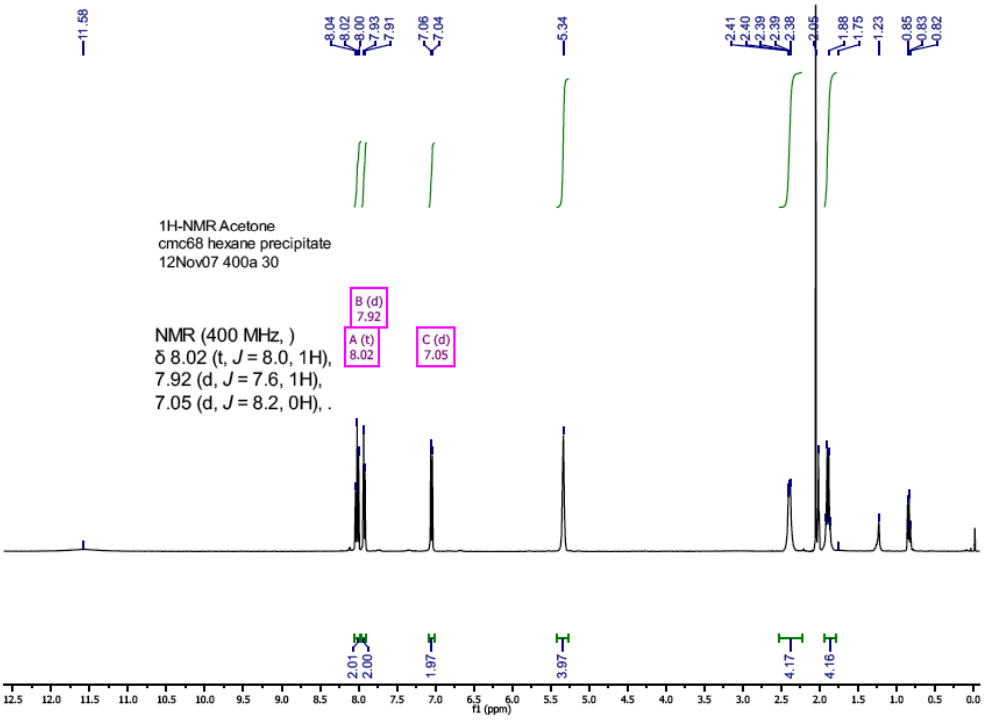

Figure S2. ^{1}H NMR spectrum of complex [Rh(**2**)(cod)]SbF$_6$ in CD$_3$COCD$_3$ at 298 K.

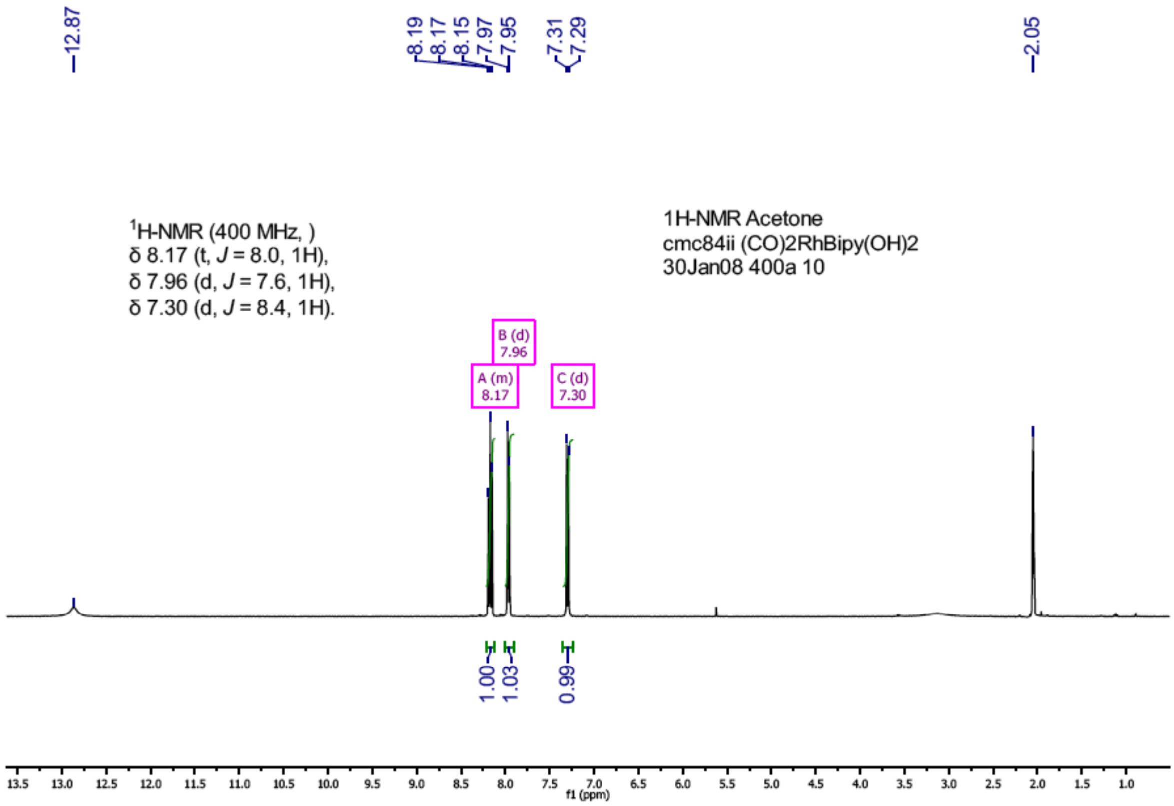

Figure S3. ^{1}H NMR spectrum of complex [Rh(**2**)(CO)$_2$]SbF$_6$ in CD$_3$COCD$_3$ at 298 K.

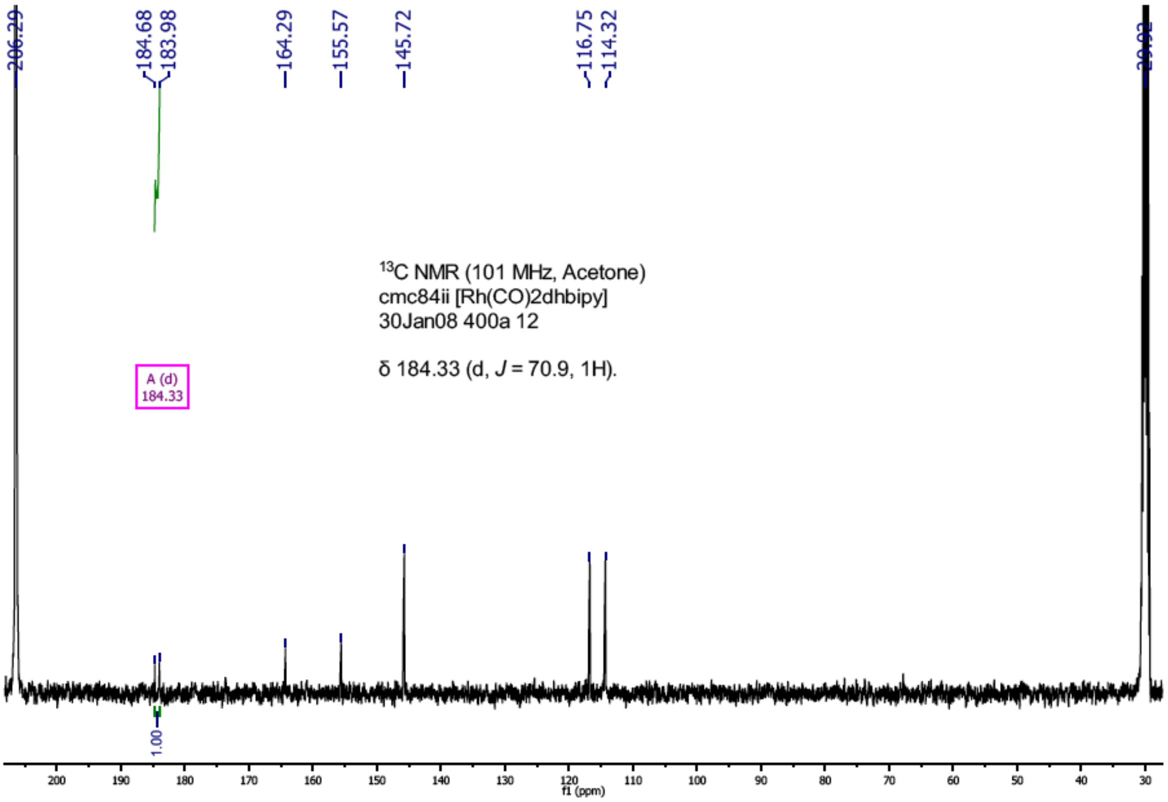

Figure S4. ^{13}C{^{1}H} NMR spectrum of complex [Rh(**2**)(CO)$_2$]SbF$_6$ in CD$_3$COCD$_3$ at 298 K.

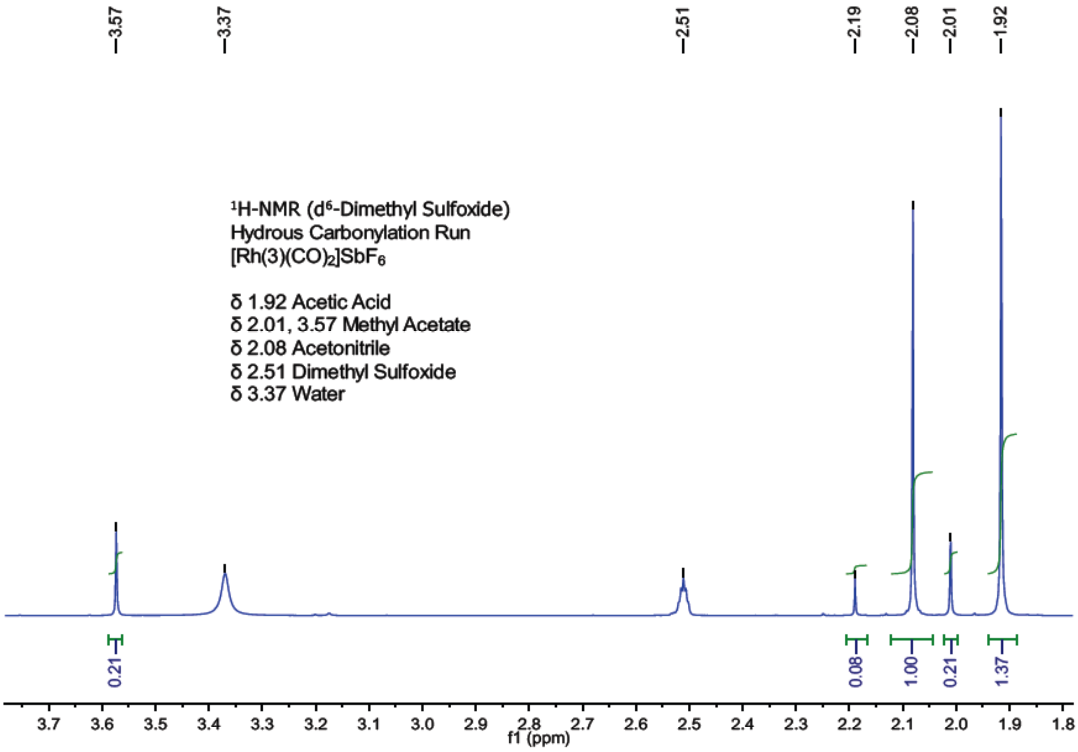

Figure S10. Example of product analysis by ^{1}H NMR for carbonylation experiment under aqueous conditions.

X-Ray Crystallography

The included solvent present in the structure of [Rh(**1**)(CO)$_2$]SbF$_6$ was found to be highly disordered, and so the SQUEEZE procedure of the PLATON program[S1] was used, suggesting 1005 electrons per unit cell, equivalent to *ca.* 503 electrons per asymmetric unit. Before the use of SQUEEZE, nine acetone and two diethylether sites had been identified in the asymmetric unit. Maintaining a similar ratio of these two solvents, the electron density was modelled as being due to 12Me$_2$CO and 3Et$_2$O (corresponding to 510 electrons), and so the contents of the asymmetric unit were adjusted on the basis of this being the solvent present. The O–H protons on O(13) and O(14) of each of the five independent complexes were not located. Combining this with the solvent removed by SQUEEZE, the unit cell contents determined from the atom list is $C_{96}H_{224}O_{30}$ lower than what is actually present. All five of the SbF$_6$ anions were found to be disordered, and in each case two orientations were identified, though only for the Sb(5) anion were two sites for the antimony located (for the other four anions the two orientations shared the same antimony position). For the Sb(1), Sb(2), Sb(3), Sb(4) and Sb(5) anions the occupancies of the two orientations were *ca.* 78:22, 59:41, 72:28, 76:24 and 57:43 respectively. In each case the major occupancy atoms were refined anisotropically, and for the Sb(5) anion the minor occupancy antimony atom was also refined anisotropically. Unsurprisingly given the amount of disorder and included solvent present in the structure, and the five independent cation:anion pairs, the crystal used for this structure determination was a weak scatterer of X-rays, as can been seen from the low observed level (12345 reflections observed out of 26538 unique, 47%). As a consequence the overall precision of the structure is lower than ideal.

References

S1 P. v.d. Sluis and A.L. Spek, *Acta Crystallogr., C*, 1990, **A46**, 194.

Figure Captions

Fig. S20 The molecular structure of one ([Rh(**1**)(CO)$_2$]SbF$_6$-**A**) of the five crystallographically independent cationic complexes present in the crystals of [Rh(**1**)(CO)$_2$]SbF$_6$ (30% probability ellipsoids).

Fig. S21 The molecular structure of one ([Rh(**1**)(CO)$_2$]SbF$_6$-**B**) of the five crystallographically independent cationic complexes present in the crystals of [Rh(**1**)(CO)$_2$]SbF$_6$.

Fig. S22 The molecular structure of one ([Rh(**1**)(CO)$_2$]SbF$_6$-**B**) of the five crystallographically independent cationic complexes present in the crystals of [Rh(**1**)(CO)$_2$]SbF$_6$ (30% probability ellipsoids).

Fig. S23 The molecular structure of one ([Rh(**1**)(CO)$_2$]SbF$_6$-**C**) of the five crystallographically independent cationic complexes present in the crystals of [Rh(**1**)(CO)$_2$]SbF$_6$.

Fig. S24 The molecular structure of one ([Rh(**1**)(CO)$_2$]SbF$_6$-**C**) of the five crystallographically independent cationic complexes present in the crystals of [Rh(**1**)(CO)$_2$]SbF$_6$ (30% probability ellipsoids).

Fig. S25 The molecular structure of one ([Rh(**1**)(CO)$_2$]SbF$_6$-**D**) of the five crystallographically independent cationic complexes present in the crystals of [Rh(**1**)(CO)$_2$]SbF$_6$.

Fig. S26 The molecular structure of one ([Rh(**1**)(CO)$_2$]SbF$_6$-**D**) of the five crystallographically independent cationic complexes present in the crystals of [Rh(**1**)(CO)$_2$]SbF$_6$ (30% probability ellipsoids).

Fig. S27 The molecular structure of one ([Rh(**1**)(CO)$_2$]SbF$_6$-**E**) of the five crystallographically independent cationic complexes present in the crystals of [Rh(**1**)(CO)$_2$]SbF$_6$.

Fig. S28 The molecular structure of one ([Rh(**1**)(CO)$_2$]SbF$_6$-**E**) of the five crystallographically independent cationic complexes present in the crystals of [Rh(**1**)(CO)$_2$]SbF$_6$ (30% probability ellipsoids).

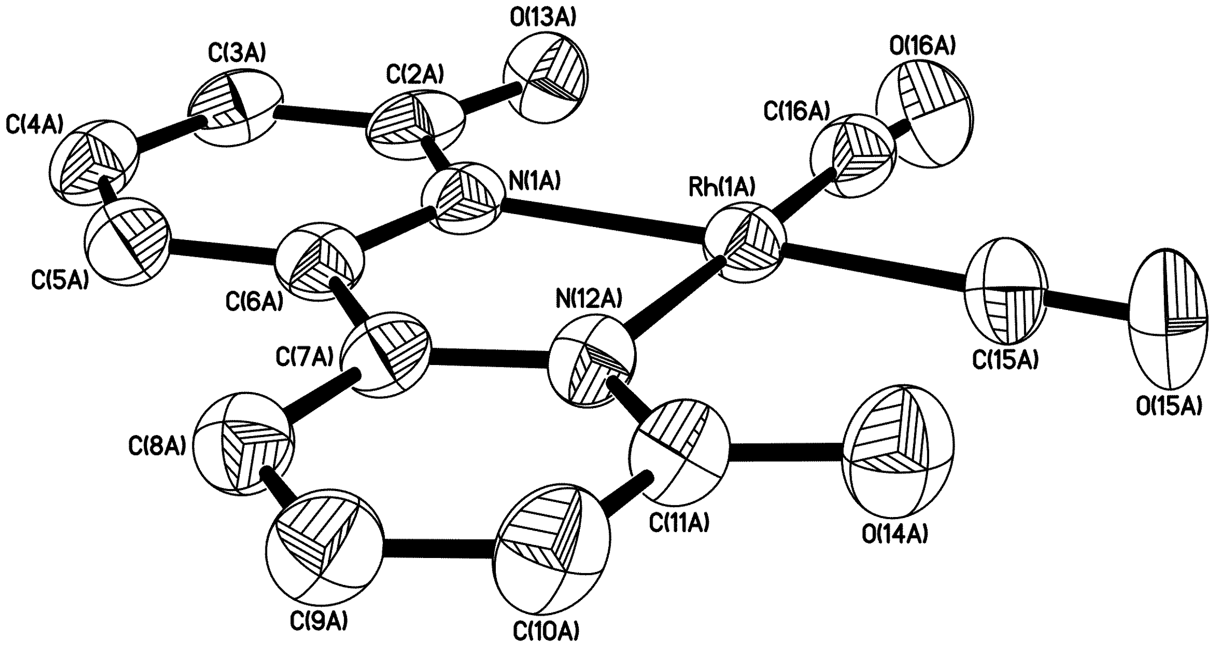

Fig. S20

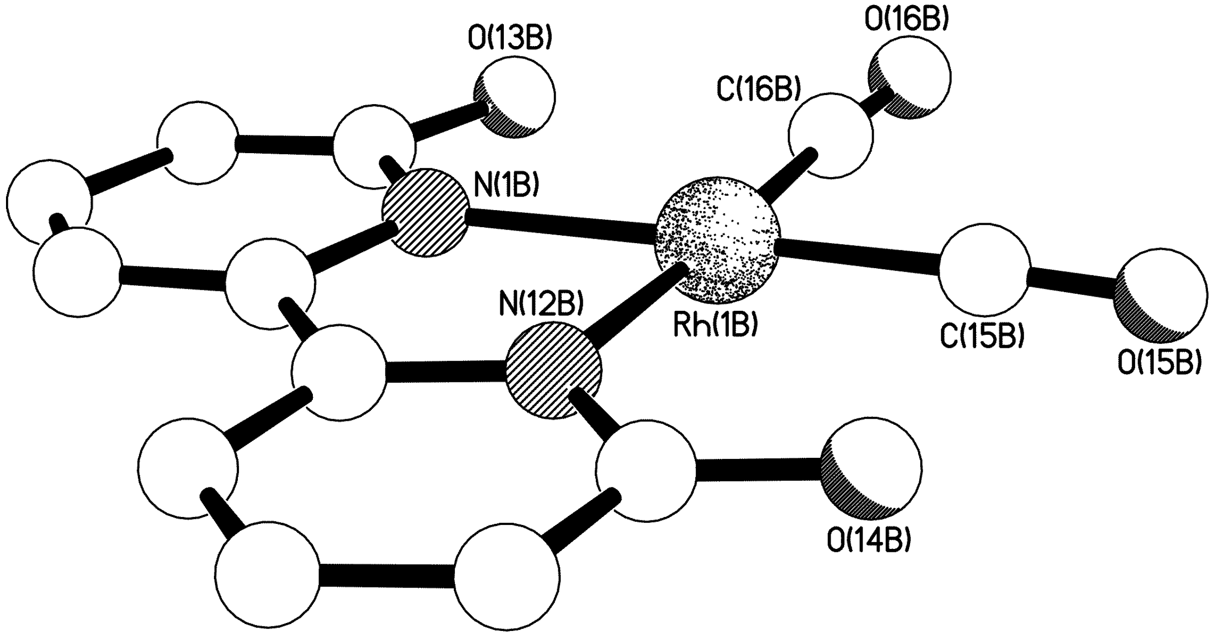

Fig. S21

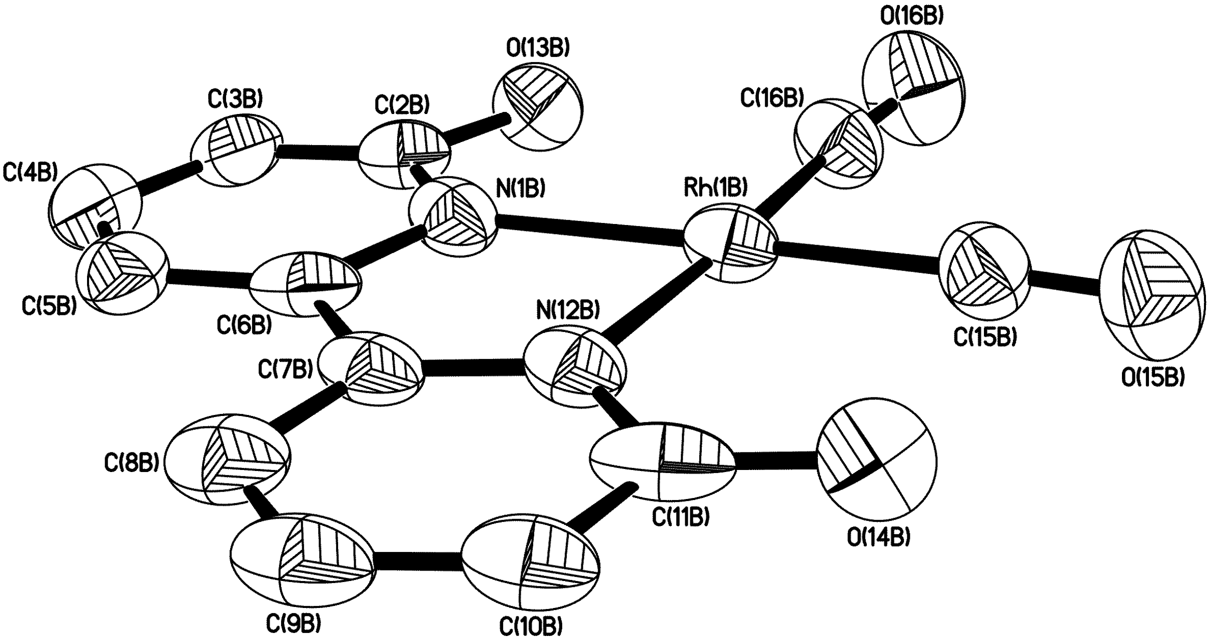

Fig. 22

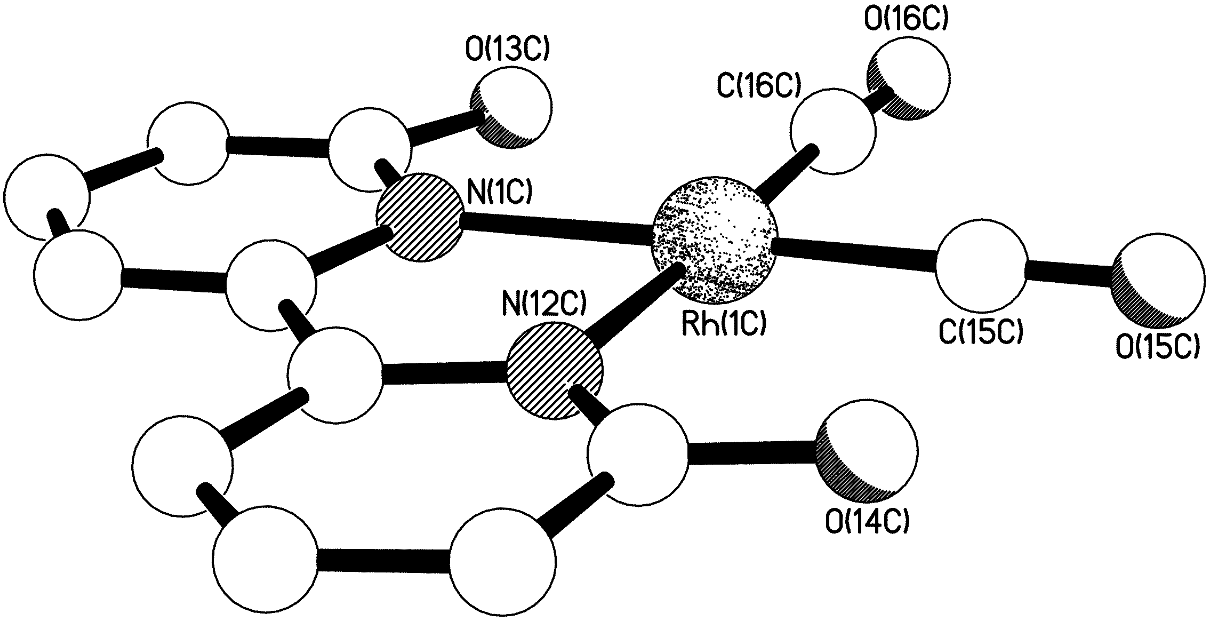

Fig. S23

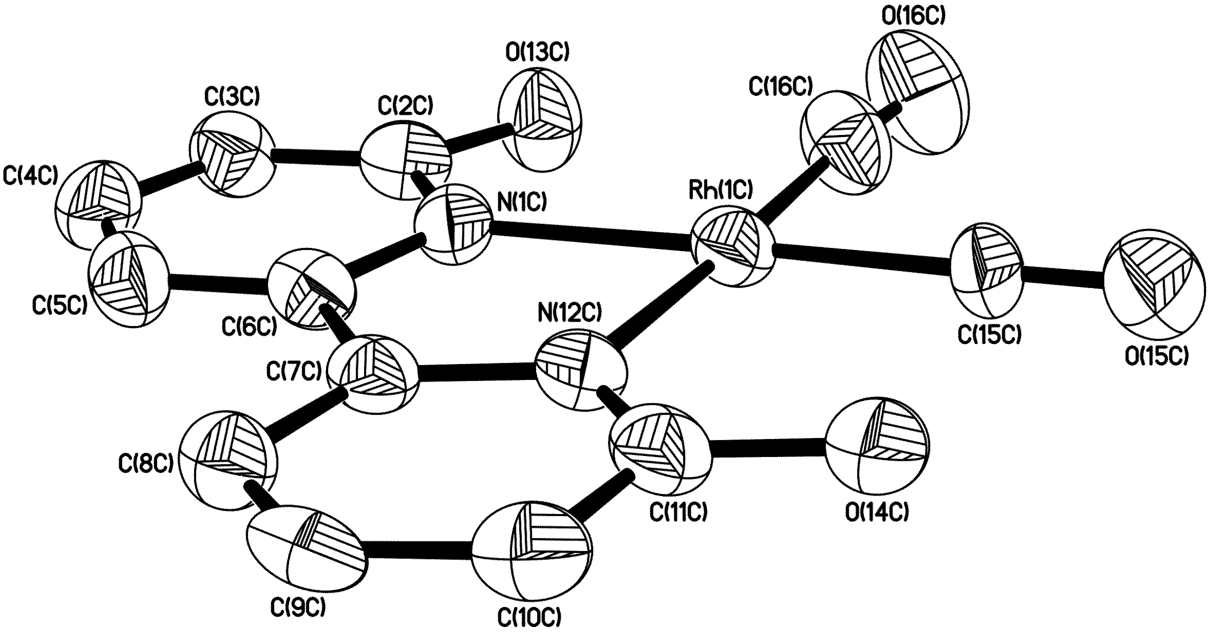

Fig. S24

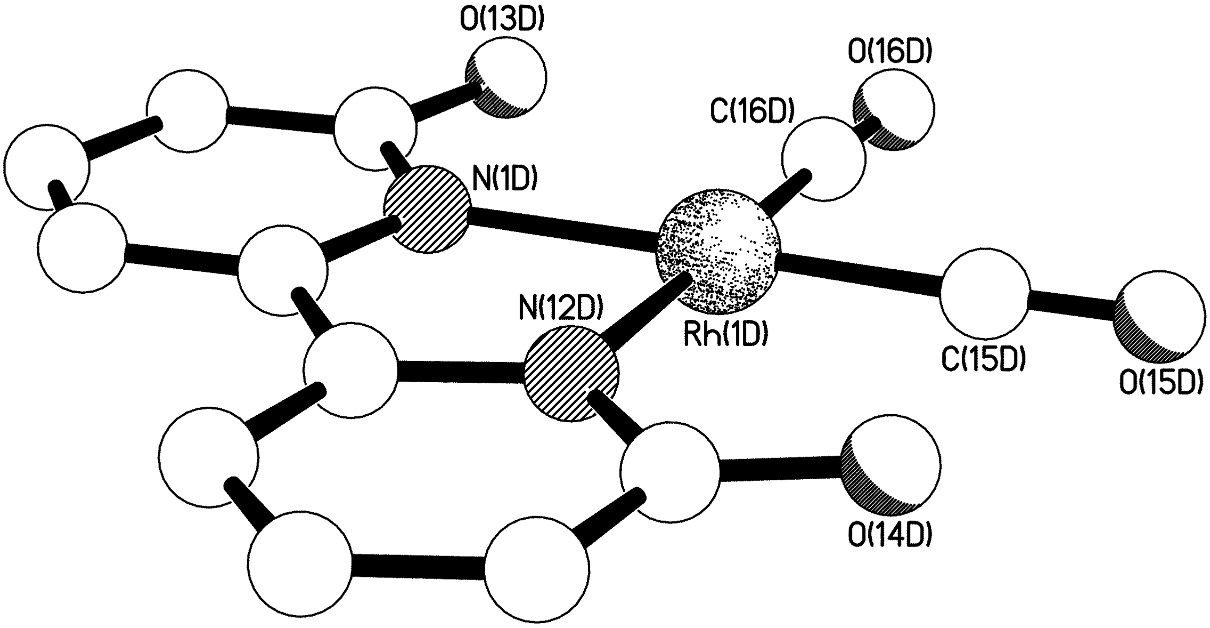

Fig. S25

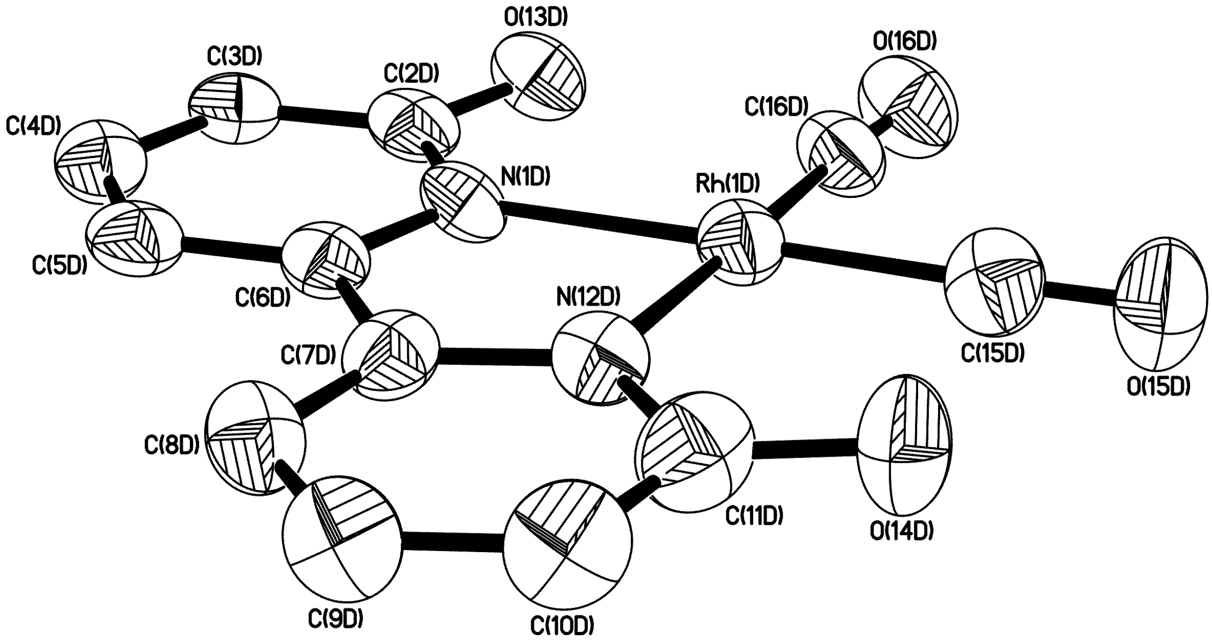

Fig. S26

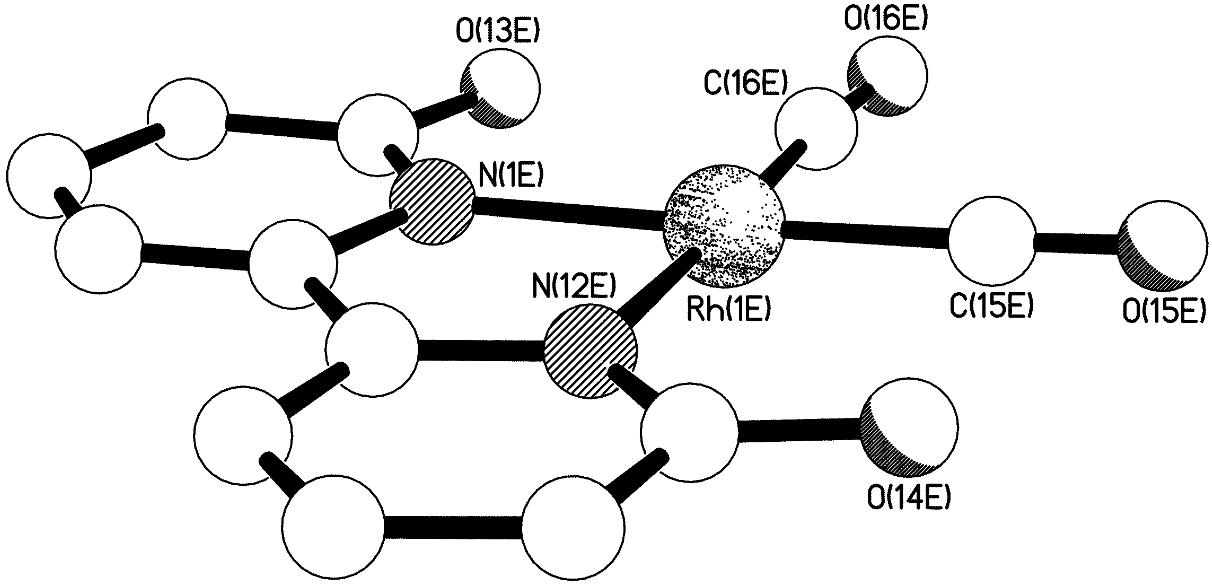

Fig. S27

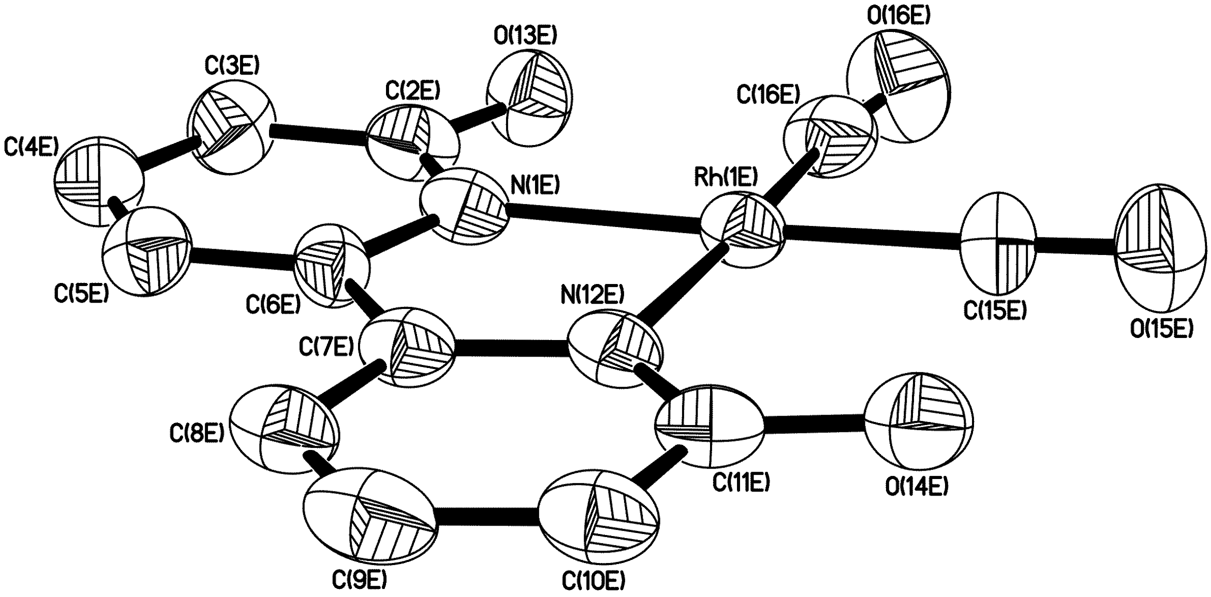
O(16E)
O(13E)
C(3E)
C(2E)
C(16E)
C(4E)
N(1E)
Rh(1E)
C(5E)
C(6E)
N(12E)
C(15E)
O(15E)
C(7E)
C(8E)
C(11E)
O(14E)
C(9E)
C(10E)

Fig. S28