RHODIUM

References

Rh⁰ 4*d*: ↑↓ ↑↓ ↑↓ ↓ ↓ | 5*s*: ↓ | 5*p*: | 5*d*: | **E.N.** 1.5

1 + (d^8) **2 + (d^7)**

Rh_2O (?) ← (−O_2) — **2 + (d^7)**

2 + (d^7) → (>1100°; H_2) → **$Rh(OH)_3$**↓ blue, strong Red agent

Rh, met., wh., ductile, d = 12.44, m.p. 1963, b.p. ~3700, corrosion resistance > Pt, slowly dissolves in conc. H_2SO_4, (HBr + NaClO) (*t*), insol. in aq. reg.; paramagn. Cub. close park., a = 3.79, Rh — Rh 2.68

↓ sputtering

Rh black, sol. in Ox acs., most active hydrogenation cat.

Rh + O_2 (800°) → Rh_2O (?)

Rh + H_2 + CO (*t*, *p*) → **M[Rh(CO)$_4$]**, **HRh(CO)$_4$**, cr., light yel., m.p. −10 with dec., mol.: tetrahedron; **Na[Rh(CO)$_2$(PPh$_3$)$_2$]** [1]; **HRh(CO)(PR$_3$)$_3$**

Rh + H_2 + CO (>−10° (−H_2)) → **$HRh(PF_3)_4$**, liq., colrl., m.p. −40, b.p. 90 with dec., sparingly sol. in H_2O, sol. in org. solvents; mol.: tetrahedron, Rh — P 2.34, 2.39; · **0.5 C_6H_6**; **K[Rh(PF$_3$)$_4$]**, cr., colrl., stab. in air; **HRh(PR$_3$)$_4$**; **$H_2RhCl(PR_3)_2$**; **Rh(NO)$^+$(PPh$_3$)$_3$** [1]; **[HRh(N$_2$)(PR$_3$)$_2$]** [1]

Rh + CO → **$Rh_2(CO)_8$**, cr., orange, hyg., m.p. 76 with dec. [12]; **[Rh$_2$(PPh$_3$)$_8$]**, cr., light grn., diamagn.; **[Rh$_2$(PF$_3$)$_8$]**, cr., orange, m.p. 93

Rh + CO (*t*) → **$Rh_4(CO)_{12}$**, cr., red, dec. 150, not reacts with H_2O, struct. analogue of $Co_4(CO)_{12}$, Rh — Rh ≈2.7, Rh — C 1.7–2.2; **Rh$_4$(CO)$_n$(PR$_3$)$_{12-n}$** [12]

$Rh_6(CO)_{16}$ (previously "$Rh_4(CO)_{11}$"), cr., blk., dec. 220, not reacts with H_2O, sparingly sol. in org. solvents; mol.: octahedral cluster [Rh_6] (Rh – Rh 2.78), μ_3-CO at 4 faces, 2 termnl. CO at vertices, cat. for P – C bond cleavage in PR_3 (⟶ RCHO + RCH_2OH); **Rh$_6$(CO)$_n$L$_{16-n}$**; **M[Rh$_6$(CO)$_{15}$]**; **M$_2$[Rh$_6$(CO)$_{14}$(SCN)$_2$]**; **M$_2$[Rh$_{10}$S(CO)$_{22}$]**; **M$_3$[Rh$_{12}$Sb(CO)$_{27}$]** [2]

Rh + CO (Ag) (*t* ⟶) → **$Rh_2(CO)_8$**

M[$Rh_5(CO)_{15}$], mol.: trig. bipyr. [1]

M$_2$[Rh$_6$(CO)$_{15}$], **M$_4$[Rh$_6$(CO)$_{14}$]** [2]

[Me$_4$N]$_3$[Rh$_7$(CO)$_{16}$], cluster [Rh_7] – single-cap octahedron, Rh — Rh 2.71–2.88, Rh — C 1.86 (termnl.), 2.01–2.48 (br.) [8]

M$_3$Rh$_9$(CO)$_{13}$ [8]; **M$_3$[Rh$_{11}$(CO)$_{23}$]** [8]

M$_2$[Rh$_{12}$(CO)$_{30}$], anion: 2 [$Rh_6(CO)_{15}$] groups [struct. analogues of $Rh_6(CO)_{16}$] bonded by 2 CO br., Rh — Rh 2.82, Rh — C 1.88 (termnl.) and 2.00 (br.) [8]

M$_2$[H$_3$Rh$_{13}$(CO)$_{24}$]; **M$_4$[Rh$_{14}$(CO)$_n$]**, n = 25, 26; **M$_3$[Rh$_{15}$(CO)$_{27}$]**; **M$_3$[Rh$_{17}$(CO)$_{30}$]**; **[R$_4$N]$_4$[Rh$_{22}$(CO)$_{37}$]**, cluster anions, Rh — Rh 2.69–2.90 [2, 23]

M[Rh(CO)$_4$]$_n$ → KOH

Li$_4$RhH$_4$; **Li$_4$RhH$_5$** [3]

Rh_2SO_4 [19], · **nH_2O**, n = 4, 12, 15

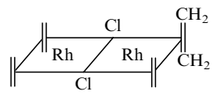
[$Rh(NH_3)_3Cl_3$]; [$Rh(NH_3)_5Cl$]Cl_2 → (*t*) → Rh

Rh + $Rh(CH_3COO)_2$ + CO + ROH + HBF_4 → **M$_2$[Rh$_6$C(CO)$_n$]**, n = 13, 15; **K[Rh$_6$N(CO)$_{15}$]**; **Cs$_2$[Rh$_9$P(CO)$_{21}$]**, C, N and P ats. – at cluster centres – octahedron or single-cap antiprism [21]

Rh + CO (*t*, *p*) → **$Rh_2(CO)_8$**

Rh + O_2 (Ag) (*t* ⟶) → **$Rh_2(CO)_8$**

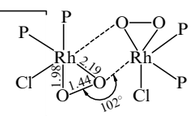
Rh + L (p = 10^5 Pa) → **[RhX(CO)$_2$]$_2$**, X = Hal, NO_3, SCN, SO_4/2, RCOO, C_5H_5, cr., Hal = Cl (orange, m.p. 123); Br (brn., 118); I (ruby red, 114), sol. in org. solvents, diamagn., mol: 2 squares with common Hal — Hal side, Rh — Rh 3.12; **[RhCl(CO)L$_2$]**, L = Py, PR_3, AsR_3, mol.: square (dsp^2), hydrogenation cat.; **[RhCl(CO)L]$_2$**, L = C_2H_4, PR_3, CO; Rh — Rh 2.81 [9]; **[RhX(CO)(PR$_3$)$_2$]**, X = OH, HCO_3, reversibly adds CO_2 [15]; **[RhCl(CS)(PPh$_3$)$_2$]**, thiocarbonyl, mol.: square [14]; **[RhCl(NO)(AsR$_3$)$_2$]**; **[RHal(NO)$_2$]$_n$**↓, Hal = Cl, Br, I, cr., dark brn.; **[RhHal$_2$(NO)(PR$_3$)$_2$]**; **RhHal(PR$_3$)$_2$**, cr., red; **[RhHal(PR$_3$)$_3$]**, cr., red, cat. of C≡C and C=C hydrogenation and aldehyde synthesis from C_nH_{2n}, H_2 and CO



[RhCl(CH$_2$=CH$_2$)$_2$]$_2$

[RhCl(PPh$_3$)$_2$(O$_2$)]$_2$, O_2 adds reversibly; ***trans*-RhCl[P(C_6H_{11})$_3$]$_2$L**, L = O_2 (cr., blue), N_2, P_4, H_2, CO, C_2H_4 (yel., diamagn.) [4]; **RhHal(PPh$_3$)$_2$(RNC)(O$_2$)**, diamagn., O_2 added reversibly (R = *n*-$CH_3C_6H_4$) or irreversibly (R = *tert*-Bu) [10]; **{Rh(O$_2$)[(Ph$_2$PCH$_2$—)$_2$]$_2$}$^+$[PF_6]$^-$**, isostruct. to Ir complex, Rh — O 2.02, O — O 1.42; O_2 added reversibly

Dioxygen complexes



{Rh[P(OMe)$_3$]$_2$}$^+$[BPh_4]$^-$, angle cation, ∠PPhP 90, Rh — P 2.18, Ph of the anion enters the coordination sphere of Rh

[Rh(CO)(PR$_3$)$_4$]$_2$S; **[Rh(CO)SP$_2$]**, octahedron and square [25]

(C$_5$H$_5$)Rh(C$_5$H$_6$); + H^+ ⟶ H_2↑ + [$Rh^{III}(C_5H_5)_2$]$^+$

$RhCl_3$ + NaC_5H_5

M$_2$[HRh(CN)$_4$(H$_2$O)]

[Rh$_2$(μ-SO$_4$)$_2$Py$_6$] · **nH_2O**, n = 3, 6; **[Rh$_2$(μ-H$_2$PO$_4$)$_4$(H$_2$O)$_2$]**, clusters, Rh — Rh 2.5–2.6 [17]; **[Rh(NO$_3$)(PPh$_3$)$_3$]ClO$_4$** [29]

[Rh(RCOO)$_2$]$_2$ (previously "$HRh^I(RCOO)_2$"), cr., grn., diamagn., struct. analogues of Cu^{II} and Cr^{II} acetates, cluster, Rh CN 5; **[Rh(CH$_3$COO)$_2$L]$_2$**, L = H_2O, ROH, PR_3, NH_3, Py, cr., grn. or blue, diamagn. cluster, Rh — Rh 2.35–2.45, struct. analogues of [Cu(CH$_3$COO)$_2$L]$_2$, Rh — O 1.99, Rh — H_2O 2.30

Br⁻, SO_2 anod. Ox → **2.5 + [Rh$_2$(CH$_3$COO)$_5$]** **[Rh$_2$(CH$_3$COO)$_4$Cl]** [22]

M$_4$[Rh$_2$(SO$_4$)$_4$(H$_2$O)$_2$] · **nH_2O**, M = Na – Cs, [H_3O], grn., Rh — Rh 2.45, all [SO_4] are br. [17]

Na$_2$[Rh(SO$_3$)$_2$] · **2 H_2O**

M$_4$[Rh$_2$(CO$_3$)$_4$] · **nH_2O**, M = Na, K (n = 2.5), Cs (n = 6.3; 7.5); NH_4 (n = 4.5), Ba/2, diamagn. clusters [16]

M$_2$[Rh$_2$(CH$_3$COO)$_4$Hal$_2$], Hal = Cl, Br, Rh — Rh 2.47, Rh — O 2.07, Rh — Hal 2.06 (Cl), 2.53 (Br) [27]

RhCl$_3$ + CO (*t*) → **$Rh_2OCl_2(CO)_3$**, needles, red, m.p. 125

RhCl$_3$ + CO + EtOH + PR_3 → **RhCl$_2$**, cr., red, ΔH = −163, Ox by air, $CdCl_2$ type struct.

RhCl$_3$ + RCHO + PR_3 → **[RhCl$_2$(CO)(PR$_3$)]**, cr., yel. [5]

RhCl$_3$ + EtOH + PR_3 → **M$_2$[Rh$_2$Hal$_4$(CO)$_2$]**, exists in H_2O soln. [13]; **H[RhCl$_2$(CO)(PR$_3$)]**; **[R$_4$N][RhHal$_2$(CO)$_2$]-*cis***, cr., yel., diamagn., stab. in HCl soln., anion: square

RhCl$_3$ + *S* (*t*) → **Rh$_9$S$_8$ RhS$_2$ RhSe$_2$ RhTe$_2$** pyrite type struct.; **Rh$_2$S$_5$ Rh$_3$S$_4$ Rh$_2$Se$_5$ Rh$_2$Te$_5$** (*t* (−S))

Rh_2P, **RhP_2**, **RhP_3**

[RhPy$_6$]Hal$_2$, Hal = Cl–I, cr., yel.; **[RhPy$_5$Hal]Hal**, Hal = Cl–I, cr., yel.; **[RhDipy$_2$ClX]$_2$**, X = NO_3, ClO_4, cr., reddish viol., diamagn.; **[Rh(AsR$_3$)$_4$Hal$_2$]**; **[Rh(AsR$_3$)$_3$Hal$_2$]$_2$**