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Synthesis and Electrochemistry of Some Homo- and Hetero-dinuclear Trihydride Complexes of Rhodium, Iron, Cobalt, and Nickel

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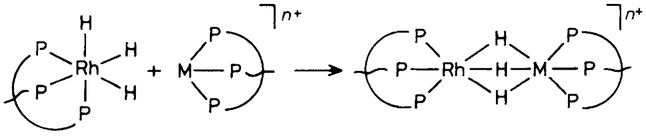
Homo- and hetero-dinuclear, diamagnetic and paramagnetic complexes of general formula $\{[MeC(CH_2PPh_2)_3]Rh(\mu\text{-}H)_3M(L)\}^{n+}$ [M = Rh, Co, Ni, L = $MeC(CH_2PPh_2)_3$; M = Fe, L = $MeC(CH_2PEt_2)_3$] have been synthesized and characterized; the electrochemical behaviour of the compounds shows that they reversibly undergo multisequential one-electron redox changes.

A large number of polynuclear polyhydride metal complexes have been prepared and characterized because of the active role these compounds play in a number of hydrogenation and C–H activation reactions.[1] Heterometal[2] and paramagnetic[2a,3,4] derivatives are of particular interest, the former for their potential synergistic properties,[5] the latter for containing formally odd-electron metal centres.[3]

Herein we report on the synthesis, characterization, and electrochemistry of some new diamagnetic and paramagnetic polyhydrides containing $[Rh(H)_3Rh]^{n+}$, $[Rh(H)_3Fe]^{n+}$, $[Rh(H)_3Co]^{n+}$, and $[Rh(H)_3Ni]^{n+}$ cores. A unique strategy has been used to synthesize the parent compounds with $[Rh(H)_3Rh]^{+}$, $[Rh(H)_3Fe]^{2+}$, $[Rh(H)_3Co]^{2+}$. and $[Rh(H)_3Ni]^{2+}$ cores respectively. This involves reaction of the mononuclear trihydride (triphos)RhH_3[6] (**1**) [triphos = $MeC(CH_2PPh_2)_3$] with electrophilic metal fragments formed by triphos or etriphos [etriphos = $MeC(CH_2PEt_2)_3$] with a metal cation (Scheme 1). Thus, reaction of (**1**) with a 0.5 : 1 : 1



M = Rh n = 1; Fe, Co, Ni n = 2

Scheme 1

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(triphos)RhH_3
(1)

[(triphos)Rh(μ-H)$_3$Rh(triphos)]$BPh_4 \cdot CH_2Cl_2$
(2)

[(triphos)Rh(μ-H)$_3$Co(triphos)]$(ClO_4)_2$
(3)

[(triphos)Rh(μ-H)$_3$Ni(triphos)]$(ClO_4)_2$
(4)

[(triphos)Rh(μ-H)$_3$Fe(etriphos)]$(BF_4)_2$
(5)

[(triphos)Rh(μ-H)$_3$Rh(triphos)]$(BPh_4)_2 \cdot$DMF
(6)

Table 1. Standard potentials (in V *vs.* standard calomel electrode) for the redox changes of the binuclear complexes in CH_2Cl_2 solution [0.1 M in $(NBu_4)ClO_4$] at 25 °C.

Compound	Redox changes		
	+3/+2	+2/+1	+1/0
(3)	+0.76	+0.17	−1.83[a]
(4)	—	−0.05	−1.15
(5)	—	−0.77	—
(6)	+0.35	−0.35	−1.34

[a] Peak potential value for an irreversible charge transfer.

mixture of $[RhCl(C_2H_4)_2]_2$, triphos, and $AgPF_6$ in CH_2Cl_2, followed by addition of $NaBPh_4$ in ethanol gives the paramagnetic complex [(triphos)Rh(μ-H)$_3$Rh(triphos)]$BPh_4 \cdot CH_2Cl_2$[7] **(2)** in 65% yield. Analogously, [(triphos)Rh(μ-H)$_3$Co(triphos)]$(ClO_4)_2$ **(3)** ($\mu_{eff.}$ 2.20 μ_B), [(triphos)Rh(μ-H)$_3$Ni(triphos)]$(ClO_4)_2$ **(4)** [$\mu_{eff.}$ 3.40 μ_B; i.r. (Nujol mull) 1685 cm$^-$ ν(Rh–H–Ni)], and [(triphos)Rh(μ-H)$_3$Fe(etriphos)]$(BF_4)_2$ **(5)** {diamagnetic; i.r. (Nujol mull) 1610 cm^{-1} ν(Rh–H–Fe); $^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2, 213 K, relative to 85% H_3PO_4) 62.86 (s, etriphos), 21.33 p.p.m. [d, *J*(P–Rh) 87 Hz, triphos]; ^1H n.m.r. (CD_2Cl_2, 293 K) δ − 13.82 (m)} are obtained by treating **(1)** and triphos with the appropriate metal^{2+} salts. Replacement of triphos with etriphos in the synthesis of **(5)** is necessary because of the poor ligating properties of triphos towards iron(II) cations.[8]

Compound **(2)** in dimethylformamide (DMF) is readily oxidized by atmospheric oxygen to give [(triphos)Rh(μ-H)$_3$Rh(triphos)]$(BPh_4)_2 \cdot$DMF **(6)** whose structure consists of two (triphos)Rh fragments linked together by three bridging hydride ligands.[7] The two rhodium atoms are separated by a short distance [2.644(1) Å]. Interestingly, **(6)** can be converted into **(2)** by reduction with $NaC_{10}H_8$. This fact, and the scarcity of electrochemical data on metal polyhydrides in the literature,[2a] prompted us to investigate the electrochemistry of these binuclear trihydrides.

The cyclic voltammetric response of **(6)** in 0·1 M $(Nbu_4)ClO_4$–CH_2Cl_2 solution is shown in Figure 1. By controlled potential coulometry, a one-electron oxidation and two subsequent one-electron reductions are observed. The appearance of a directly associated peak at ΔE_p value of *ca.* 60 mV in the reverse scan for each electrode step indicates that the species electrogenerated are stable, at least on the time scale of cyclic voltammetry, and maintain the molecular framework of the starting +2 derivative. Therefore we can represent the redox change occurring in the anodic process as +2/+3, and the two redox changes involved in the cathodic process as +2/+1 and +1/0. Analogously, the heterometal derivatives **(3)** and **(4)** exhibit the consecutive redox changes +2/+3, +2/+1, +1/0 (irreversible), and +2/+1, +1/0, respectively. Compound **(5)** gives rise only to +2/+1 charge-transfer, followed by decomposition of the +1 species. Table 1 summarizes the standard potentials of all the redox changes observed in CH_2Cl_2 solution for these trihydrides.

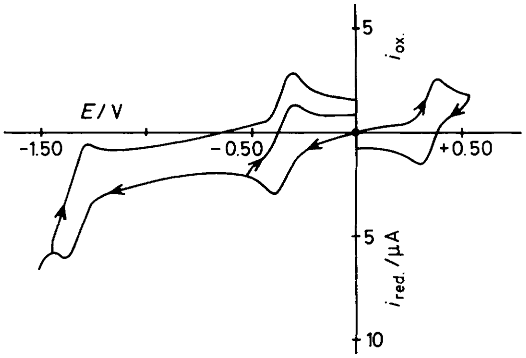

Figure 1. Cyclic voltammogram recorded at a platinum electrode in a CH_2Cl_2 solution containing **(6)** (2.2×10^{-4} mol dm^{-3}) and $(NBu_4)ClO_4$ (0·1 mol dm^{-3}). Scan rate: 0.2 v s^{-1}. (●) Starting potential.

We have also synthesized the following derivatives: [(triphos)Rh(μ-H)$_3$Rh(triphos)]$(BF_4)_3$ {diamagnetic; i.r. (Nujol mull) 1650 cm^{-1} ν(Rh–H–Rh); $^{31}P\{^1H\}$ n.m.r. (CD_3COCD_3, 213 K) 37.09 p.p.m. [d, *J*(P–Rh) 97 Hz, triphos]}, [(triphos)Rh(μ-H)$_3$Co(triphos)]ClO_4 [$\mu_{eff.}$ 3.38 μ_B; i.r. (Nujol mull) 1650 cm$^-$ ν(Rh–H–Co)], [(triphos)Rh(μ-H)$_3$Co(triphos)]$(BF_4)_3$ [diamagnetic; i.r. (Nujol mull) 1650 cm^{-1} ν(Rh–H–CO)], and [(triphos)Rh(μ-H)$_3$Ni(triphos)]ClO_4 (μ_{eff} = 2.02 μ_B). The oxidations and reductions were carried out in CH_2Cl_2 solution using $NOBF_4$ as oxidant and $NaBH_4$ as reducing agent. All of the compounds obtained are crystalline solids. Preliminary *X*-ray analyses of **(4)** and [(triphos)Rh(μ-H)$_3$Co(triphos)]ClO_4 suggest that the cations have the same geometry as **(6)**.[7,9]

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