Inorganica Chimica Acta, *155* (1989) 49–53

Chemical and Electrochemical Oxidation of a Series of *p*-Tolylformamidinatedirhodium(I) Complexes

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(Received May 9, 1988)

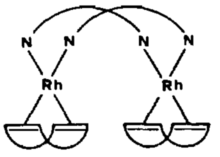
Abstract

The electrochemical behaviour of the dirhodium(I) complexes $Rh_2(COD)_2(form)_2$ (**1**), $Rh_2(COD)(CO)_2(form)_2$ (**2**) and $Rh_2(CO)_4(form)_2$ (**3**) (COD = 1,5-cyclooctadiene; form = CH_3-*p*-C_6H_4–NC(H)N–C_6H_4-*p*-CH_3) has been investigated in non-aqueous solvent. All the complexes undergo sequential anodic processes, which ultimately involve deep reorganizations of the starting frame. However, in all cases a first one-electron removal leading to the corresponding $[Rh_2]^{3+}$ monocation is observed. These monocations, which are fully stable in the timescale of cyclic voltammetry, slowly decompose after their chemical obtainment with a timelife ranging from about 30 min for $[\mathbf{2}]^+$ to a few minutes for $[\mathbf{3}]^+$. Complete characterization of the monocations has been performed. In contrast with **1**–**3**, $Rh_2(COD)_2(CH_3COO)_2$ undergoes only fast framework-destroying anodic processes.

Introduction

Interest in the electrochemistry of dirhodium(I) complexes is increasing. Recent papers have dealt with the redox behavior of complexes having the two metal centres connected by different ligands, such as isocyanides [1–3], two-bridging phosphino and/or arsino molecules of A-frame type [4–8] and μ-phosphido species [9].

In the course of our studies on the synthesis of formamidinato complexes having $[Rh_2]^{n+}$ cores (n = 4 [10, 11], 5 [12]), the mechanism with which the dirhodium(I) complex $[Rh(COD)(RNC(H)NR)]_2$ (COD = 1,5-cyclooctadiene; R = C_6H_4-*p*-CH_3) [13] undergoes chemical oxidation by silver salts remained obscure. With this in mind, we present here the redox chemistry of the dirhodium(I) complexes **1**–**3** of general formula $[Rh_2(form)_2(CO)_{4-2n}(COD)_n]$ (n = 0, 1, 2; form = CH_3-*p*-C_6H_4–NC(H)N–C_6H_4-*p*-CH_3).



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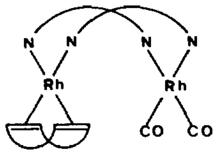

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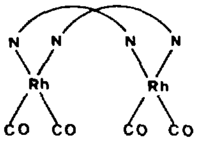

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Electrochemical studies of some related dirhodium(I) compounds appeared just recently, namely $[Rh(COD)(\mu\text{-}pz)]_2$ (pz = pyrazolate) [14], $[Rh(COD)(RNNNR)]_2$ (R = C_6H_4-*p*-CH_3) [15], $[Rh_2(RNNNR)_2(CO)_{4-2n}(PPh_3)_n]$ (R = C_6H_4-*p*-CH_3; n = 0, 1) [15], $[Rh_2(RNC(Me)NR)_2(CO)_{4-n}(PPh_3)_n]$ (R = Ph; n = 0, 1, 2) [15], $[Rh_2(RNNNR)_2(CO)_2(bipy)]$ (R = C_6H_4-*p*-CH_3; bipy = 2,2′-bipyridyl) [16], $[Rh_2(\mu\text{-}porphinato)(CO)_4]$ [17].

Interestingly, among a series of analogous diiridium(I) complexes studied also from the electrochemical viewpoint [14, 18–21], the redox chemistry of $[Ir(RNC(H)NR)(COD)]_2$ (R = C_6H_4-*p*-CH_3) has been recently elucidated [22].

Results and Discussion

Electrochemistry

Figure 1 illustrates the cyclic voltammetric behavior of **1**–**3** in dichloromethane solution. As can be seen, all complexes display a series of sequential redox changes, which make the complete elucidation of the relevant pathways rather complicated, mainly because of the chemical irreversibility of some steps. A common feature is however present in all the responses: a first oxidation process at peak A, which, exhibiting a directly associated reduction peak B in the reverse scan, preludes to a chemical reversibility of the relevant redox change.

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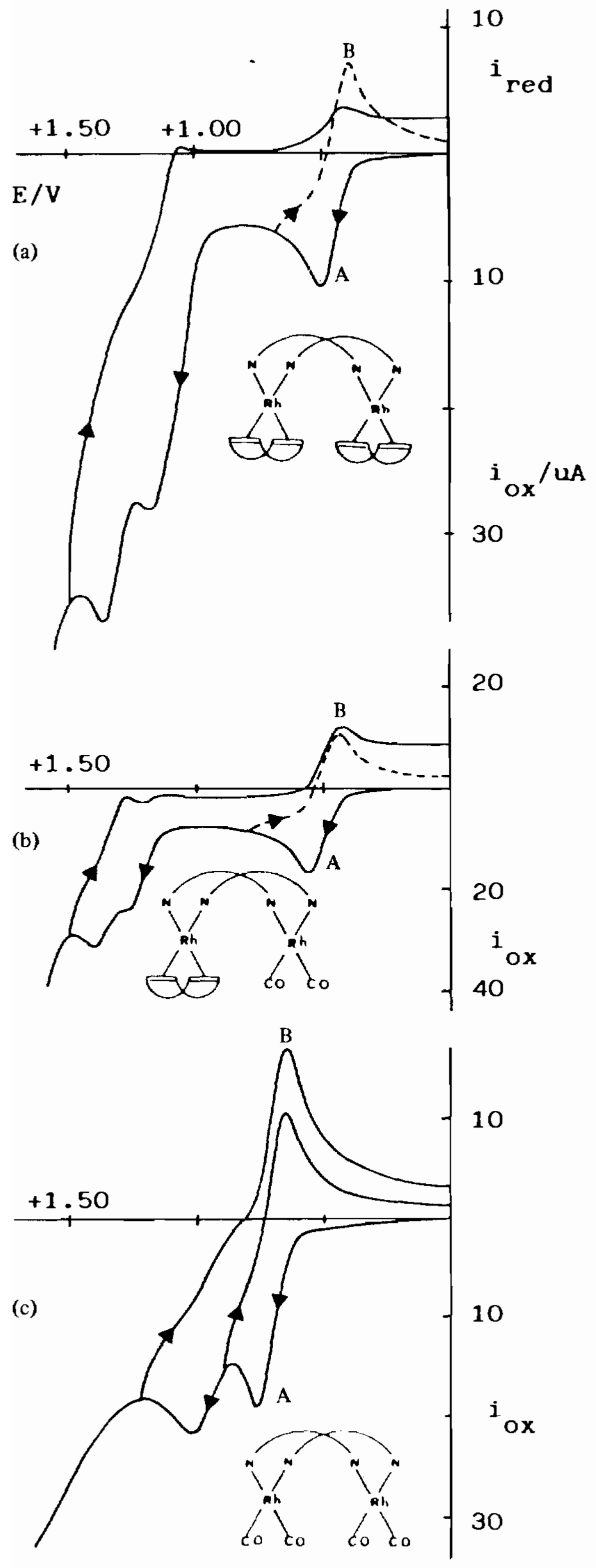

Fig. 1. Cyclic voltammograms recorded in CH_2Cl_2 solutions containing $[NBu_4]ClO_4$ (0.1 mol dm^{-3}) and (a) **1** (7.8 × 10^{-4} mol dm^{-3}); (b) **2** (8.8 × 10^{-4} mol dm^{-3}); (c) **3** (9.3 × 10^{-4} mol dm^{-3}). Scan rate 0.2 V s^{-1}.

Controlled potential coulometry has shown that in all the three derivatives this first process involves a one-electron oxidation.

The analysis of the cyclic voltammetric responses relevant to the peak system A/B with scan rate [23] (gradually increasing from 0.02 V s^{-1} to 20 V s^{-1}) reveals essentially the same features for **1**–**3**: the ratio i_{pB}/i_{pA} is constantly equal to 1; the term $i_{pA}v^{-1/2}$ remains constant; the difference $E_{pA} - E_{pB}$ increases from 80 mV at the slowest scan rate to 350 mV at the highest scan rate. These parameters are diagnostic for the occurrence of an uncomplicated quasireversible one-electron oxidation step.

On the contrary different pathways hold in the successive oxidations of the dirhodium derivatives. Merely based on the relative peak heights we can indicate qualitatively that: (i) $[\mathbf{1}]^+$ undergoes a two-electron process ($E_p = +1.19$ V), the irreversibility of which suggests deep reorganizations within the molecular framework, followed in turn by a one-electron step ($E^{\circ\prime} = +1.20$ V) with some extent of reversibility; (ii) $[\mathbf{2}]^+$ undergoes an irreversible one-electron process ($E_p = +1.27$ V), followed also in this case by a successive one-electron oxidation not completely irreversible ($E^{\circ\prime} = +1.33$ V); (iii) $[\mathbf{3}]^+$ undergoes an irreversible one-electron process ($E_p = +1.04$ V), followed by ill-defined oxidations. This picture testifies to our difficulty in establishing the step-by-step pathway which leads from **1** to different formamidinato–dirhodium complexes by oxidation with silver salts [10–12]. However we point out here that the first step involves the generation of the corresponding monocation, this being true also in the case of complexes **2** and **3**.

Table 1 summarizes the standard electrode potentials of the redox change neutral/monocation in **1**–**3**. For comparison the redox potentials of the same anodic step in similar rhodium and iridium derivatives are also reported. From these data the following conclusions can be drawn: (i) the gradual substitution of COD molecules for CO groups in **1**–**3** makes the removal of electrons more and more difficult, so indicating that COD is less electron-withdrawing than CO; (ii) the formamidinate group is certainly a better σ-donor ligand than triazenide and carboxylate (see later): hence the presence of such ligand favours the thermodynamic access to $[Rh_2]^{3+}$ mixed-valence species, which are, very likely, the precursors of the $[Rh_2]^{4+}$ and $[Rh_2]^{5+}$ derivatives obtained by chemical oxidation of **1** with AgO_2CCF_3 (molar ratio 1:3) [10] and $AgNO_3$ [12], respectively; (iii) the redox potentials of iridium and rhodium complexes bearing the same ligands follow a normal trend taking into account that iridium is more easily oxidized than rhodium.

TABLE 1. Redox Potentials (in volts, *vs.* SCE) for the One-electron Oxidation of some Dirhodium(I) Complexes

Complex	$E^{\circ\prime}$ (Rh(I)Rh(I)/Rh(I)Rh(II))	Solvent	Reference
$Rh_2(COD)_2$(pyrazolate)$_2$	+0.45^a	THF	14
$Ir_2(COD)_2$(pyrazolate)$_2$	+0.38	CH_2Cl_2	20
$Rh_2(COD)_2$(*p*-tolyl-triazenido)$_2$	+0.53	CH_2Cl_2	15
$Rh_2(COD)_2$(*p*-tolyl-formamidinate)$_2$	+0.47	CH_2Cl_2	present work
$Ir_2(COD)_2$(*p*-tolyl-formamidinate)$_2$	+0.47	THF	22
$Rh_2(COD)(CO)_2$(*p*-tolyl-formamidinate)$_2$	+0.51	CH_2Cl_2	present work
$Rh_2(CO)_4$(*p*-tolyl-triazenido)$_2$	+0.83	CH_2Cl_2	15
$Ir_2(CO)_4$(*p*-tolyl-triazenido)$_2$	+0.71	CH_2Cl_2	21
$Rh_2(CO)_4$(phenyl-acetamidinate)$_2$	+0.47	CH_2Cl_2	15
$Rh_2(CO)_4$(*p*-tolyl-formamidinate)$_2$	+0.72	CH_2Cl_2	present work
$Rh_2(CO)_4$(tetraphenylporphinato)	+0.78^a	CH_2Cl_2	17
$Rh_2(CO)_4$(octaethylporphinato)	+0.66^a	CH_2Cl_2	17

^{a}Peak potential value for irreversible process.

Characterization of the Monocations

Controlled potential exhaustive one-electron oxidation on a red–brown dichloromethane solution of 2 (working potential +0.7 V) leads to a green solution, whose cyclic voltammogram is quite similar to that reported in Fig. 1b, except the peak system A/B is now reversed, in that it corresponds to a reduction process. Figure 2 shows the X-band ESR spectra recorded on this electrogenerated species $[2]^+$ both at room and liquid nitrogen temperature.

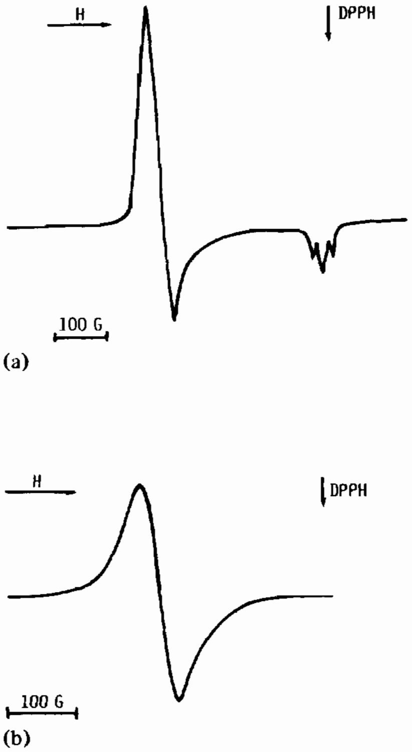

Fig. 2. X-band ESR spectra of the electrochemically generated monocation $[2]^+$ in CH_2Cl_2–$[NBu_4]ClO_4$ (0.1 mol dm^{-3}): (a) 100 K; (b) 300 K.

The well resolved spectrum at 100 K exhibits strongly anisotropic behavior and it is indicative of an axial structure characterized by $g_\perp$ and $g_\parallel$ values of 2.209 and 2.016, respectively. The lineshape analysis shows that the high-field adsorption is structured in a 1:2:1 pattern ($a_\parallel = 18.7$ G) resulting from the interaction of one unpaired electron with an overall nuclear spin system equal to 1. This means that the aIS hyperfine term in the electron Hamiltonian of the dirhodium moiety (^{103}Rh, 100%; $I = 1/2$) can be explained taking into account a strong electron delocalization over the two rhodium nuclei. It is, therefore, not unlikely that the electron removal leads to a metal–metal bond formation in the electrogenated d^8–d^7 system, as happens for the one-electron oxidation of the somewhat similar complex $Rh_2(CO)_2(PPh_3)_2$(*p*-tolyl-triazenido)$_2$ [24].

At room temperature the ESR spectrum evolves to a single isotropic adsorption centred at $g_{iso} = 2.158$ ($\Delta H_{iso} = 53.3$ G).

The green monocation $[2]^+$ can also be obtained by chemical oxidation by reacting 2 with $AgPF_6$ (molar ratio 1:1) in dichloromethane solution. The composition of the microcrystalline solid [(COD)-Rh(form)$_2$Rh(CO)$_2$]PF_6 has been established by analytical data, conductivity measurements, and its spectral IR and ESR patterns. The molar conductance value of a 10^{-4} M dichloromethane solution indicates that the complex behaves as a 1:1 electrolyte, while the IR spectrum displays (nujol mull) two absorptions at 2060 and 2100 cm^{-1}, which are readily attributed to terminal *cis* carbonyl groups, and a strong band at 1565 cm^{-1} due to the asymmetric N═══C═══N stretching frequency. The shift to higher frequencies of the ν(CO) bands with respect to those of the starting complex (1990 and 2060 cm^{-1}) provides evidence for the increased formal oxidation number of the dirhodium moiety. On the contrary $\nu(N{=\!=\!=}C{=\!=\!=}N)$ seems barely dependent on the formal oxidation number of the metals (1560 cm^{-1} in the starting Rh(I) complex, 1570 cm^{-1} in the Rh(II) derivative $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ [10]).

The complex $[2]^+$ is stable as a solid, but in dichloromethane solution it decomposes in a period of 30 min (even less in other solvents) giving a red solution. Infrared spectra recorded of this species over this time show the appearance of two $\nu(CO)$ bands due to the regeneration of the starting neutral complex. The ^1H NMR spectra confirm this behavior. In fact while the signals of a freshly prepared dichloromethane solution of $[2]^+$ are very broad, the same signals sharpen with time indicating that paramagnetic species are no longer present.

When the oxidation of the starting complex 2 is performed with a molar ratio 1:2 the complex $[2]^+$ is still obtained.

Electrogeneration of the green monocation $[1]^+$ in dichloromethane solution can be performed by macroelectrolysis at +0.55 V. Cyclic voltammogram on this exhaustively oxidized solution displays a reduction process just coincident with the peak system B/A reported in Fig. 1a. Frozen ESR spectra recorded immediately after completion of the electrolysis show a relatively broad adsorption pattern similar to that previously discussed ($g_\perp = 2.066$; $g_\parallel = 1.961$), but with the presence of minor amounts of unidentified paramagnetic fragments.

Chemical oxidation of an orange dichloromethane solution of **1** by $AgPF_6$ (in molar ratio 1:1) affords instantaneously the green solution of $[(COD)Rh(form)]_2PF_6$. This monocation is however even less stable than $[2]^+$, and the green colour of the solution disappears within about 15 min, turning to yellow–orange.

We have been unable to characterize this yellow–orange product, nevertheless we can exclude the presence of paramagnetic species owing to the very sharp signals displayed in the ^1H and ^{31}P NMR spectra. It is not unlikely that Rh(I) and Rh(III) species are present in the yellow–orange product. The same results have been found during the oxidation of **1** with AgO_2CCF_3 (molar ratio 1:1) [10].

The behavior of the tetracarbonyl derivative $[Rh(form)(CO)_2]_2$ with $AgPF_6$ (molar ratio 1:1) was similar to that of $[Rh(C_8H_{12})(form)]_2$ and $(C_8H_{12})Rh(\mu\text{-}form)_2Rh(CO)_2$ but the green colour, attributable to the monocation $[Rh(form)(CO)_2]_2PF_6$, disappears in a few minutes. This agrees with the fact that the solution of **3** exhaustively one-electron oxidized is ESR silent. From these results it is possible to conclude that the stability of the mono-oxidized species increases in the order $[(C_8H_{12})Rh(\mu\text{-}form)_2Rh(CO)_2]^+ > [Rh(C_8H_{12})(form)]_2^+ > [Rh(form)(CO)_2]_2^+$.

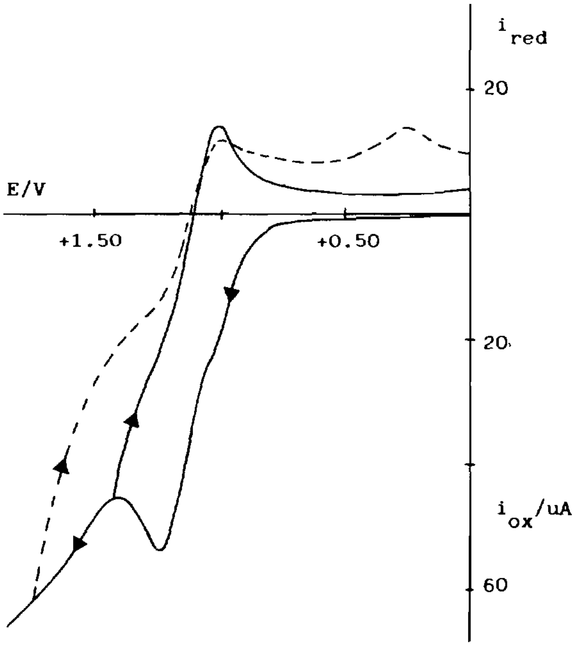

Fig. 3. Cyclic voltammogram recorded at a platinum electrode on a CH_2Cl_2 solution containing $Rh_2(COD)_2(O_2CCH_3)_2$ (2.3×10^{-3} mol dm^{-3}) and $[NBu_4]ClO_4$ (0.1 mol dm^{-3}). Scan rate 0.2 V s^{-1}.

A further evidence of the stability of the monocations $[1]^+$–$[3]^+$ in the cyclic voltammetric time scale lies in the fact that the cyclic voltammetric response A/B is completely unaffected by the presence of a CO atmosphere.

It is finally worth noticing that we never succeeded in synthesizing $[Rh_2]^{n+}$ ($n \neq 2$) cores by chemical oxidation with silver salts of $[Rh(COD)(O_2CCH_3)]_2$. In this connection Fig. 3 shows the cyclic voltammetric behavior of $[Rh(COD)(O_2CCH_3)]_2$. It gives rise to an anodic process involving two merging one-electron steps, complicated by following chemical reactions. ESR tests on solutions resulting from macroelectrolysis at +1.3 V gave evidence that no paramagnetic species was formed.

It is possible that the failure of the acetate complex to act as precursor in the synthesis of dirhodium(II) complexes is correlated to its inability to give the monocation $[Rh(COD)(O_2CCH_3)]_2^+$.

Experimental

Starting Materials

$[Rh(C_8H_{12})(form)]_2$ (**1**) and $[Rh(form)(CO)_2]_2$ (**3**) were prepared by literature procedures [13]. Silver hexafluorophosphate and chromium hexacarbonyl were purchased from Aldrich Chemie and used as received. The supporting electrolyte tetrabutylammonium perchlorate $[NBu_4]ClO_4$ (Fluka) was dried in a vacuum oven and used without further purification. Dichloromethane solvent for electrochemistry (Burdick and Jackson) was of 'distilled in glass' grade and used as received.

Apparatus

The apparatus for spectroscopic and electrochemical techniques has been previously described [11]. Potential values (measured at 20 ± 0.1 °C) are referred to an aqueous saturated calomel reference electrode (SCE). Under the present experimental conditions the ferrocenium/ferrocene couple was located at +0.49 V.

Synthesis of $(C_8H_{12})Rh(\mu\text{-}form)_2Rh(CO)_2$ (2)

$[Rh(C_8H_{12})(form)]_2$ (0.4 g, 0.46 mmol) was suspended in n-heptane and $Cr(CO)_6$ (0.2 g, 0.92 mmol) was added. The mixture was heated to reflux for 3 h. The red solution obtained was filtered through a short celite column (to remove some metal formed) and the solvent evaporated *in vacuo*. The red solid residue was dissolved in benzene, and the solution chromatographed on a neutral alumina column saturated with n-hexane. n-Hexane was used as eluant to give the desired compound in a 43% yield. *Anal.* Calc. for $Rh_2N_4O_2C_{40}H_{42}$: C, 58.83; H, 5.18; N, 6.87. Found: C, 58.79; H, 5.28; N, 6.87%. IR (Nujol mull, cm^{-1}): 1990s, 2060s, 1560vs. ^1H NMR ($CDCl_3$, 30 °C): δ 2.21s, 2.25s.

Synthesis of $[(C_8H_{12})Rh(\mu\text{-}form)_2Rh(CO)_2]PF_6$ ($[2]^+$)

A solution of $(C_8H_{12})Rh(\mu\text{-form})_2Rh(CO)_2$ (0.25 g, 0.3 mmol) dissolved in 10 ml of dichloromethane was combined with $AgPF_6$ (0.77 g, 0.3 mmol) dissolved in a few drops of acetone. The colour of the solution immediately changed from red to green and was accompanied by the formation of a grey precipitate of silver metal. After 10 min the resultant solution was filtered on a short celite column and evaporated to dryness. The green solid obtained was washed with n-hexane and quickly crystallized from benzene giving 0.12 g of compound. *Anal.* Calc. for $Rh_2N_4O_2PF_6C_{40}H_{42}$: C, 49.96; H, 4.40; N, 5.82; P, 3.32. Found: C, 49.33; H, 4.57; N, 5.95; P, 3.34%. IR (Nujol mull, cm^{-1}): 2060s, 2100s, 1565vs. Conductivity (Λ, $cm^2\ mol^{-1}\ \Omega^{-1}$ in 10^{-4} M solution in dichloromethane): 48.

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