Journal of Organometallic Chemistry, 204 (1991) 413–420
Elsevier Sequoia S.A., Lausanne
JOM 21414

Electrochemistry of the pyrazolate-bridged dirhodium(I) complex $Rh_2(CO)_2(PPh_3)_2(\mu\text{-}3,5\text{-}Me_2pz)_2$

Renato Seeber and Giovanni Minghetti

Dipartimento di Chimica, Università di Sassari, Via Vienna 2, 07100 Sassari (Italy)

Maria I. Pilo

Istituto per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici-CNR, Via Vienna 2, 07100 Sassari (Italy)

Guido Banditelli

Dipartimento di Chimica Inorganica e Metallorganica, Centro CNR, Università di Milano, Via Venezian 21, 20133 Milano (Italy)

Silvia Zamponi

Dipartimento di Scienze Chimiche, Università di Camerino, Via S. Agostino 1, 62032 Camerino (Italy)

(Received June 26th, 1990)

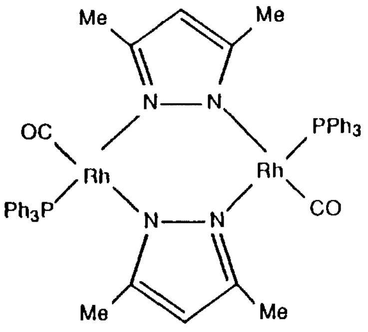
Abstract

The dirhodium(I) complex $Rh_2(CO)_2(PPh_3)_2(\mu\text{-}3,5\text{-}Me_2pz)_2$ undergoes two consecutive oxidation processes at a platinum electrode in dichloromethane. The first oxidation gives the corresponding cationic species, $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}3,5\text{-}Me_2pz)_2]^+$, as inferred from the electrochemical (voltammetric and coulometric) and spectroelectrochemical data and from spectroscopic (IR, ESR and visible) examination of the oxidized product. The more anodic process involves poisoning adsorptions on the electrode surface, which rules out any effective study. Suggestions concerning the electronic charge distribution inside the monocationic compound are advanced on the basis of the voltammetric and ESR data.

Introduction

The chemistry of rhodium(I) complexes containing pyrazole or substituted pyrazole ligands has been investigated in recent years, and complexes with neutral ligands and with pyrazolato anions have been described [1,2]. The anionic ligands have been shown to be able to act either as monodentate or as bidentate bridging donors, the nature of the substituents as well as the steric requirements of the coligands determining which of these coordination modes operates.

0022-328X/91/$03.50



(1)

Among the dinuclear species, the complex $Rh_2(CO)_2(PPh_3)_2(\mu\text{-}3,5\text{-}Me_2pz)_2$, where $3,5\text{-}Me_2pzH$ = 3,5-dimethylpyrazole (**1**), which we described previously [1], belongs to a series of rhodium(I) derivatives which have attracted much attention in respect of their potential reactivity at the two metal centres [3–5]. An iridium(I) analogue, $Ir_2(COD)_2(\mu\text{-}pz)_2$ [6] was found to be a catalyst in the hydroformylation of alkynes [7] and is now commercially available (Aldrich).

Because of the continuous interest in mixed-valence derivatives [8], we decided that it would be of interest to make an electrochemical investigation of the behaviour of complex **1**, in which the two metal atoms are connected by unsaturated units. In contrast to those for dirhodium complexes having the metal in +2 or higher oxidation states, reports of electrochemical properties of compounds containing the Rh_2^{2+} core are fairly scarce [9–13]. The possibility of electrochemically generating Rh_2^{3+} and Rh_2^{4+} species, more or less stable depending on the nature of the substituents, has been emphasized. Various approaches to the definition of the electronic charge distribution inside the Rh_2^{3+} core have been adopted. Although a great deal of effort has been devoted to this purpose, mainly on the basis of ESR data, most authors conclude that the assignement of individual oxidation states to the two metal centres is not justified in the absence of definitive bonding studies.

Experimental

The title compound was made as described previously [1].

Dichloromethane (Aldrich, anhydrous, 99 + %, Gold Label, water < 0.005%, packaged under nitrogen) was used as the electrochemical solvent without further purification. Tetraethylammonium tetrafluoroborate (Fluka) used as the supporting electrolyte was dried for 48h at 50 ° C in a vacuum oven before use.

Voltammetric experiments were performed either with a BAS (Bioanalytical System) CV 1B voltammograph or with a home-made electrochemical system consisting of a potentiostat, a function generator, and a digital voltmeter. Linear sweep and cyclic voltammograms were recorded with an AMEL Model 863 XY recorder. An AMEL Model 552 potentiostat connected to an AMEL Model 558 integrator was used in controlled potential coulometric tests.

Since there was no particular advantage in using high potential scan rates in voltammetric measurements, these were performed in the electrochemical cell used for the coulometric studies, i.e. an H-shaped cell with a sintered glass disk interposed between anodic and cathodic compartments. The working electrodes were a platinum disk (diameter of about 2 mm) in the voltammetric experiments and a large-area platinum-gauze basket in the electrolysis experiments, respectively. The auxiliary electrode was a mercury pool and the reference electrode was a saturated calomel electrode (SCE). Measurements were performed both at 0 ° C and at room temperature. All electrochemical experiments were carried out under 99.99% pure nitrogen.

Spectroelectrochemical measurements were performed at 0 ° C in order to avoid evaporation of the volatile solvent during the time-consuming potentiostatic tests. The optically transparent thin layer electrode (OTTLE) cell used was similar to that described in Ref. 14. The working electrode, a 80 : 20 platinum : rhodium alloy mesh (80 l.p.i.), was sandwiched between two microscope slides and the path length (0.2–0.3 mm) was fixed by Teflon spacers. The electrode assembly was held together by a Teflon frame without use of any epoxy glue. Solution volumes of 50 μl were typically used. The spectra, in the wavelength range 350–500 nm, were recorded using a Hewlett Packard Model 8452 diode array spectrophotometer. They were typically recorded either under potentiostatic conditions or during low-rate potential scans (0.5 mV s^{-1}). The data were collected and processed by an Olivetti M28 personal computer and plotted by use of a Calcomp M84 digital plotter. Nernst's plots were obtained from a graph of the potential versus $\log[Ox]_{solution}/[Red]_{solution}$. The $\log[Ox]_{solution}/[Red]_{solution}$ ratios were computed from the absorbance values measured at λ_{max} of the band of the electrode product (400 nm), in potentiostatic tests performed at progressively increasing potentials in the region where the i/E response is recorded, after a polarization time long enough for attainment of equilibrium conditions in the solution [15].

X-band ESR spectra were recorded on a Bruker ER 220D SRL spectrometer.

Results and discussion

Two $Rh_2(CO)_2(PPh_3)_2(\mu\text{-}3,5\text{-}Me_2pz)_2$ isomers can be made. The *trans* isomer was isolated pure by crystallization but the *cis* isomer was obtained only in a *cis–trans* mixture [1]. Electrochemical measurements have been performed on both the *trans* isomer and the *cis–trans* mixture, and gave identical results. In particular, the anodic portion of cyclic voltammetric curves recorded either on solutions of the *trans* isomer or of the *cis–trans* mixture, shows an anodic–cathodic peak system with exactly the same location on the potential axis and reversibility characteristics. This finding rules out the possibility that any fast chemical reaction (e.g. isomerization) is coupled (preceeding or following) with the charge transfer step, and indicates that the two isomers show identical behaviour from both a thermodynamic (standard potential values) and kinetic point of view (heterogeneous kinetics, i.e. reversibility degree of the charge transfer, as well as stability of the electrolysis product). The coincidence of the two standard potential values can be accounted for in terms of the environment around the metal centres, the CO and PPh_3 ligands

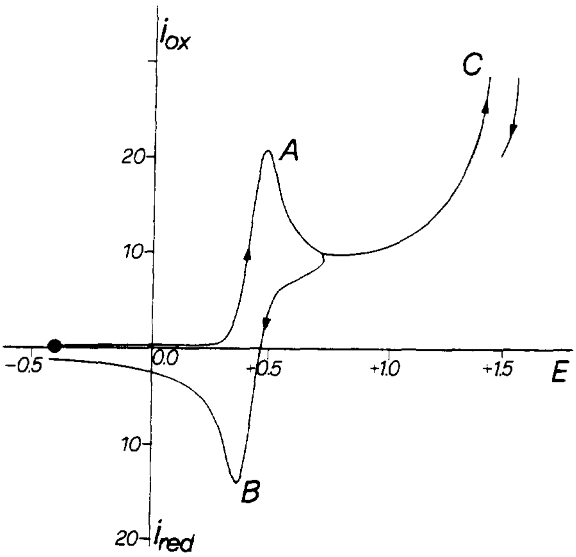


Fig. 1. Cyclic voltammetric responses for a 1.5×10^{-3} *M* $Rh_2(CO)_2(PPh_3)_2(\mu\text{-}3,5\text{-}Me_2pz)_2$, 0.1 *M* tetraethylammonium tetrafluoroborate, CH_2Cl_2 solution. Platinum working microelectrode; ● starting potential; scan rate 0.2 V s^{-1}; room temperature. Potential (E in V) is referred to SCE. Current (i) in μA.

being *trans* to quite similar moieties in the two isomers. This conclusion is supported by the IR data, the two isomers showing the ν(CO) absorptions in the same range [1]. Unless otherwise specified, the results discussed below were obtained with the complex in the *trans* form.

Figure 1 shows typical cyclic voltammetric curves recorded with a solution of $Rh_2(CO)_2(PPh_3)_2(\mu\text{-}3,5\text{-}Me_2pz)_2$ and 0.1 *M* tetraethylammonium tetrafluoroborate in CH_2Cl_2. An anodic–cathodic peak system (A/B), typical of a quasi-reversible ($\Delta E_p = 120$ mV) redox process [16], is observed. A further oxidation, occurring in correspondence to an ill-defined, poorly reproducible, anodic response (C) can also be detected. No cathodic process takes place in the potential range available in our solvent medium.

Controlled potential coulometric tests at a working potential of $+0.60$ V (peak A) allowed us to show that one mole of electrons per mole of starting compound is involved in the oxidation at peak A. During the electrolysis the solution turns from yellow to green, typical of the Rh_2^{3+} core [11]. In the cyclic voltammetric curves recorded on the one-electron oxidized solution, the same cathodic–anodic A/B peak system is present; peak B is now detected on the direct cathodic scan starting at the electrolysis potential while peak A is recorded on the backward anodic scan. Accordingly, reduction of the oxidized solution at 0.00 V leads to quantitative regeneration of the starting compound, through the consumption of one mole of electrons per mole of substance.

The results of voltammetric and coulometric tests strongly suggest the formation at peak A of a stable Rh_2^{3+} complex, bearing the same ligand set as the Rh_2^{2+} starting compound. An $E^r_{1/2}$ value of 0.430 ± 0.010 V versus SCE (at 0 °C),

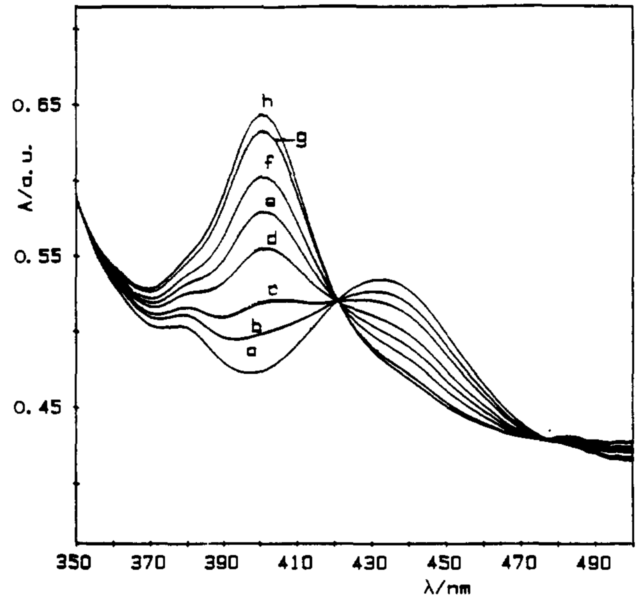


Fig. 2. Series of spectra recorded with an OTTLE cell during an anodic potential scan (0.5 mV s^{-1}) on a 10^{-3} *M* $Rh_2(CO)_2(PPh_3)_2(\mu\text{-}3,5\text{-}Me_2pz)_2$, 0.1 *M* tetraethylammonium tetrafluoroborate, CH_2Cl_2 solution; air as reference. Potential values (V vs SCE): *a*: 0.000; *b*: +0.500; *c*: +0.550; *d*: +0.600; *e*: +0.625; *f*: +0.650; *g*: +0.700; *h*: +0.800. Uncompensated *iR* drop is present.

computed as the half-sum of anodic and cathodic peak potentials [16] of A/B system, can be estimated for the Rh_2^{3+}/Rh_2^{2+} redox couple.

The data from spectroelectrochemical tests support these conclusions. Figure 2 shows spectra recorded at the indicated potential values during an anodic continuously varying potential scan up to a value at which the process is diffusion-controlled. An absorption band with a maximum at $\lambda = 432$ nm, typical of the starting compound, progressively decreases and a band with the maximum at $\lambda = 400$ nm, due to the oxidized product, progressively increases. An isosbestic point between the two bands can be clearly seen. An analogous spectral sequence is recorded on a reverse scan, taking into account that uncompensated ohmic drop causes a shift on the potential axis. Qualitatively similar sequences of spectra are also recorded by raising the potential stepwise at values progressively increasing according to a staircase waveform, as well as at different times in a single potential step at a value corresponding to diffusion-controlled conditions. In these cases analogous sequences are also obtained irrespective of whether one starts with the reduced or the oxidized form of the complex. The formal potential, $E^{\circ\prime}$, computed by spectroelectrochemical tests (Nernst's plot) at a temperature of 0 °C is $+0.420 \pm 0.010$ V versus SCE, a value compatible with $E_{1/2}^{r}$ evaluated by cyclic voltammetry.

No useful information about the process involved at peak C can be gained from the electrolysis experiments: the current falls quickly to very low values, suggesting that adsorption phenomena poisoning the electrode surface are operative.

In order to allow better characterization of the one-electron oxidation product, the CH_2Cl_2 solvent was removed by rotary evaporation and ESR measurements

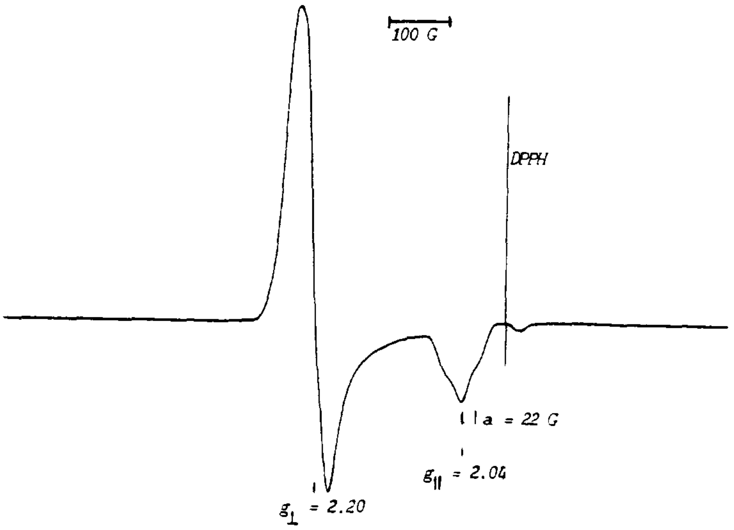


Fig. 3. ESR spectrum of compound $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}3,5\text{-}Me_2pz)_2]^+$ recorded on the frozen CH_2Cl_2 solution at 160 K. 1 G $= 10^{-4}$ T.

performed on the residue containing a large excess of supporting electrolyte. The spectrum provides evidence of a paramagnetic species but, since there is no resolution to show hyperfine structure, gives no information about the environment of the metal centres. A more significant spectrum was obtained for the frozen CH_2Cl_2 solution, and is shown in Fig. 3. At 160 K the spectrum displays anisotropic behaviour with g values of 2.04 and 2.20. Hyperfine splitting of the parallel absorption into a triplet, $a = 22$ G, can be attributed to spin-coupling to two rhodium nuclei (^{103}Rh, natural abundance 100%, $I = 1/2$). Overall the spectrum closely resembles that previously reported for a similar Rh_2^{3+} species, $[Rh_2(COD)_2(\mu\text{-}3,5\text{-}Me_2pz)_2]^+$, obtained by chemical oxidation with $NOBF_4$. The spectrum was taken as a clear evidence for delocalization of the unpaired electron spin over the two metal centres [17].

Attempts to isolate the oxidized species in a pure form have failed, owing to its ready transformation into other species. However, treatment of the crude product with water to remove the supporting electrolyte gave a solid which retained the green colour of the oxidized species; crystallization from CH_2Cl_2/Et_2O mixture did not give a wholly pure substance, but useful information was gained from its IR spectra and elemental analyses. The IR spectrum in the range 4000–600 cm^{-1} is very similar to that of the starting compound, showing the presence of the same ligands; an additional broad band, with a maximum around 1050 cm^{-1}, confirms the presence of a BF_4^- anion. The elemental analysis data (C, H, N) are consistent with a ratio between the ligands (at least phosphine/pyrazolate) similar to that in the starting compound. The whole of the available data on the oxidation product supports the formation, at peak A, of the complex $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}3,5\text{-}Me_2pz)]^+BF_4^-$.

Some indication of the extent of charge delocalization within the dinuclear system in the mixed-valence Rh_2^{3+} species can be inferred from the voltammetric behaviour of the Rh_2^{2+} complex. In principle the oxidation of a dinuclear Rh_2^{2+} complex should take place through two consecutive one-electron steps, leading to Rh_2^{3+} and to Rh_2^{4+} cores, respectively. Depending on the relative values of $E°$'s for the couples Rh_2^{3+}/Rh_2^{2+} and Rh_2^{4+}/Rh_2^{3+}, the species Rh_2^{3+} is more or less stable towards disproportionation:

$$2Rh_2^{3+} \rightleftharpoons Rh_2^{2+} + Rh_2^{4+}$$

If the electrode charge transfers involved are reversible, the fact that the equilibrium written above is shifted either towards the mixed-valence complex or in the opposite direction, implies the appearance in voltammetric experiments of either of two distinct one-electron responses or of a single two-electron peak, respectively. In the former case, the extent of separation between the two peaks can be quantitatively related to the value of the disproportionation equilibrium constant [16]; in its turn, this quantity is a measure of the delocalization of the charge in the mixed-valence complex, indicating whether the electronic configuration inside the Rh_2^{3+} core is more appropriately represented either by a Rh^{2+}–Rh^{1+} or by a $Rh^{1.5+}$–$Rh^{1.5+}$ formulation *. Though in our case the second oxidation is affected by adsorption, as well as by possible chemical reactions coupled to the charge transfer, which prevent precise thermodynamic significance being given to the location of the more anodic response on the potential axis, its separation from the less anodic peak (about 1.0 V) is large enough to suggest strong delocalization of charge in the mixed-valence species. It must be emphasized that this conclusion does not necessarily imply a direct metal–metal interaction [18–20], since pyrazolate bridges may constitute effective electronic charge carriers between the metal centres. Evidence for electronic communication between two metal centres via orbital interaction with the bridging ligands, has been given recently for similar pyrazolate complexes of iridium [21].

Acknowledgement

Financial support from C.N.R. (Rome). R.A.S. (Regione Autonoma Sardegna) and M.P.I. (Rome) is acknowledged.

References

1 G. Banditelli, A.L. Bandini, F. Bonati and G. Minghetti, J. Organomet. Chem., 218 (1981) 229.

2 S. Trofimenko in S.J. Lippard (Ed.), Prog. Inorg. Chem., Vol. 34, J. Wiley, New York, 1986, p. 115.

3 J. Powell, A. Kuksis, S.C. Nyburg and W.W. Ng, Inorg. Chim. Acta, 64 (1982) L211.

4 F. Barcelo, P. Lahuerta, M.A. Ubeda, C. Foces-Foces, F.H. Cano and M. Martinez Ripoli, J. Chem. Soc., Chem. Commun., (1985) 43; Organometallics, 7 (1988) 584.

5 T.G. Schenck, C.R.C. Milne, J.F. Sawyer and B. Bosnich, Inorg. Chem., 24 (1985) 2338.

6 K.A. Beveridge, G.W. Bushnell, K.R. Dixon, D.T. Eadie, S.R. Stobart, J.L. Atwood and M.J. Zaworotko, J. Am. Chem. Soc., 104 (1982) 920.

7 L.A. Oro, M.T. Pinillos, M. Rojo and E. Pastor, J. Chem. Research (S), (1984) 206.

---

* A large potential difference between two consecutive one-electron oxidation steps indicates a strong interaction between the two electron-exchanging sites within the molecule; in contrast, when there is no interaction between the redox centres, a single voltammetric peak is observed, resulting from two merged one-electron charge transfers [16].

8 C. Creutz, in S.J. Lippard (Ed.) Prog. Inorg. Chem., Vol. 30, J. Wiley, N.Y., 1983, p. 1 and refs. therein.
9 N.G. Connelly, G. Garcia and J.S. Stirling, J. Chem. Soc., Dalton Trans., (1987) 1403.
10 W.E. Geiger, T. Gennett and W.K. McVicar, Organometallics, 6 (1987) 1634.
11 D.C. Boyd, P.A. Matsch, M.M. Mixa and K.R. Mann, Inorg. Chem., 25 (1986) 3331.
12 C.L. Yao, J.E. Anderson and K.M. Kadish, Inorg. Chem., 26 (1987) 2725.
13 L.J. Tortorelli, C. Woods, and A.T. McPhail, Inorg. Chem., 29 (1990) 2726.
14 S. Zamponi, M. Di Marino, A. Czerwinski, and R. Marassi, J. Electroanal. Chem., 248 (1988) 341.
15 W.R. Heineman, F.M. Hawkridge, and H.N. Blount, in A.J. Bard (Ed.), Electroanalytical Chemistry, Vol 13, M. Dekker Inc., New York, 1984.
16 G. Bontempelli, F. Magno, G.A. Mazzocchin, and R. Seeber, Ann. Chim. (Rome), 79 (1989) 103.
17 D.O. Fjeldsted and S.R. Stobart, J. Chem. Soc., Chem. Comm., (1985) 908.
18 M.B. Robin and P. Day, Adv. Inorg. Chem. Radiochem., 10 (1967) 247.
19 R.R. Gagnè, C.A. Koval, T.J. Smith, and M.C. Cimolino, J. Am. Chem. Soc., 101 (1979) 4571.
20 R.S. Drago, M.J. Desmond, B.B. Corden, and K.A. Miller, J. Am. Chem. Soc., 105 (1983) 2287.
21 G.W. Bushnell, D.O.K. Fjeldsted, S.R. Stobart, M.J. Zaworotko, S.A.R. Knox and K.A. Macpherson, Organometallics, 4 (1985) 1107.